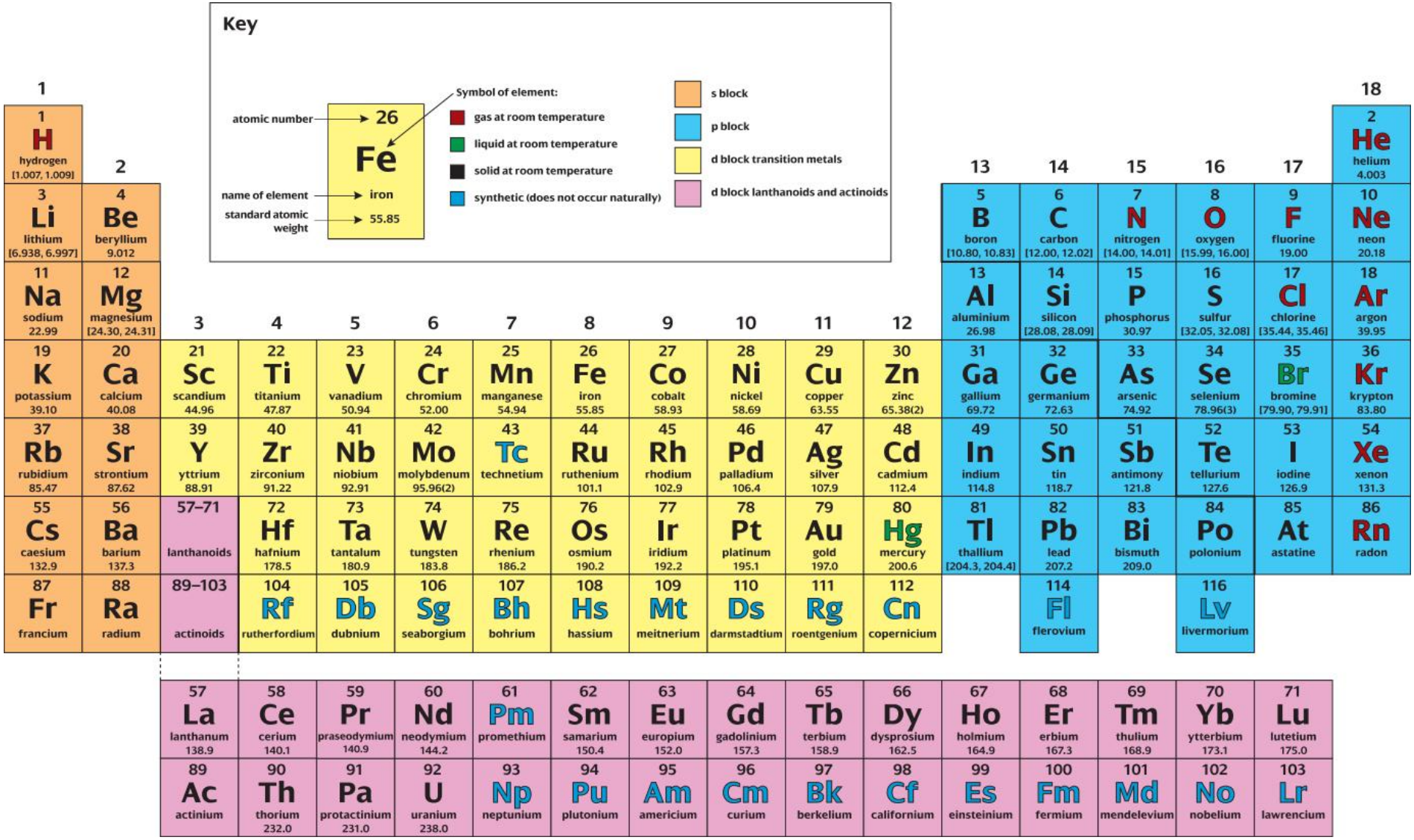
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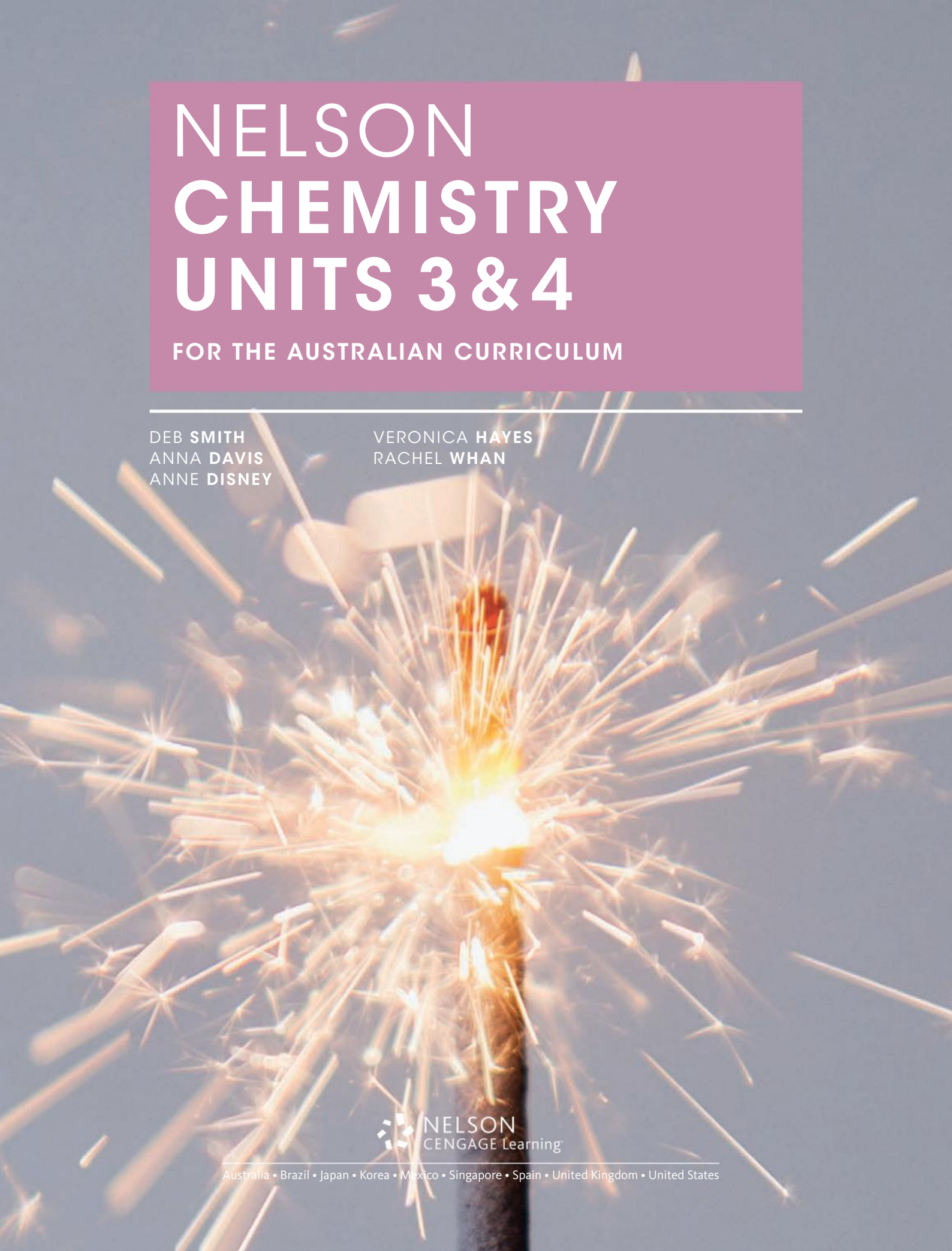
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ANNE **DISNEY**

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RACHEL **WHAN**


Key
atomic number
26
Fe
Symbol of element:
name of element
iron
standard atomic weight
55.85
gas at room temperature
liquid at room temperature
solid at room temperature
synthetic (does not occur naturally)
s block
p block
d block transition metals
d block lanthanoids and actinoids
1
18
1 H hydrogen [1.007, 1.009]
2 He helium 4.003
2
13
14
15
16
17
3 Li lithium [6.938, 6.997]
4 Be beryllium 9.012
5 B boron [10.80, 10.83]
6 C carbon [12.00, 12.02]
7 N nitrogen [14.00, 14.01]
8 O oxygen [15.99, 16.00]
9 F fluorine 19.00
10 Ne neon 20.18
11 Na sodium 22.99
12 Mg magnesium [24.30, 24.31]
3
4
5
6
7
8
9
10
11
12
13 Al aluminium 26.98
14 Si silicon [28.08, 28.09]
15 P phosphorus 30.97
16 S sulfur [32.05, 32.08]
17 Cl chlorine [35.44, 35.46]
18 Ar argon 39.95
19 K potassium 39.10
20 Ca calcium 40.08
21 Sc scandium 44.96
22 Ti titanium 47.87
23 V vanadium 50.94
24 Cr chromium 52.00
25 Mn manganese 54.94
26 Fe iron 55.85
27 Co cobalt 58.93
28 Ni nickel 58.69
29 Cu copper 63.55
30 Zn zinc 65.38(2)
31 Ga gallium 69.72
32 Ge germanium 72.63
33 As arsenic 74.92
34 Se selenium 78.96(3)
35 Br bromine [79.90, 79.91]
36 Kr krypton 83.80
37 Rb rubidium 85.47
38 Sr strontium 87.62
39 Y yttrium 88.91
40 Zr zirconium 91.22
41 Nb niobium 92.91
42 Mo molybdenum 95.96(2)
43 Tc technetium
44 Ru ruthenium 101.1
45 Rh rhodium 102.9
46 Pd palladium 106.4
47 Ag silver 107.9
48 Cd cadmium 112.4
49 In indium 114.8
50 Sn tin 118.7
51 Sb antimony 121.8
52 Te tellurium 127.6
53 I iodine 126.9
54 Xe xenon 131.3
55 Cs caesium 132.9
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76 Os osmium 190.2
77 Ir iridium 192.2
78 Pt platinum 195.1
79 Au gold 197.0
80 Hg mercury 200.6
81 Tl thallium [204.3, 204.4]
82 Pb lead 207.2
83 Bi bismuth 209.0
84 Po polonium
85 At astatine
86 Rn radon
87 Fr francium
88 Ra radium
89–103 actinoids
104 Rf rutherfordium
105 Db dubnium
106 Sg seaborgium
107 Bh bohrium
108 Hs hassium
109 Mt meitnerium
110 Ds darmstadtium
111 Rg roentgenium
112 Cn copernicium
114 Fl flerovium
116 Lv livermorium
57 La lanthanum 138.9
58 Ce cerium 140.1
59 Pr praseodymium 140.9
60 Nd neodymium 144.2
61 Pm promethium
62 Sm samarium 150.4
63 Eu europium 152.0
64 Gd gadolinium 157.3
65 Tb terbium 158.9
66 Dy dysprosium 162.5
67 Ho holmium 164.9
68 Er erbium 167.3
69 Tm thulium 168.9
70 Yb ytterbium 173.1
71 Lu lutetium 175.0
89 Ac actinium
90 Th thorium 232.0
91 Pa protactinium 231.0
92 U uranium 238.0
93 Np neptunium
94 Pu plutonium
95 Am americium
96 Cm curium
97 Bk berkelium
98 Cf californium
99 Es einsteinium
100 Fm fermium
101 Md mendelevium
102 No nobelium
103 Lr lawrencium



NELSON CHEMISTRY UNITS 3&4

FOR THE AUSTRALIAN CURRICULUM

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PREFACE

Nelson Chemistry for the Australian Curriculum Units 3 & 4 has been written to meet the requirements of the Australian Curriculum, Assessment and Reporting Authority (ACARA) Australian Senior Secondary Curriculum – Chemistry.

Nelson Chemistry for the Australian Curriculum Units 3 & 4 is written by classroom teaching experts. They were chosen for their comprehensive knowledge of the chemistry discipline and best teaching practice in chemistry education at secondary and tertiary levels. They have written the text to make it accessible, readable and appealing to students. The text has been written to enable students to meet the A level Achievement Standard. It also allows all students to maximise their learning and results.

The textbook has been written to focus on the human endeavour aspect of chemistry and highlights the relevance of chemistry to students. By providing a contextual base in the form of context chapters, this book provides reasons for developing the understanding and skills in the ACARA Australian Senior Secondary Curriculum – Chemistry.

One aim of structuring the book in this manner is to 'develop students' interest and appreciation in chemistry and its usefulness in helping to explain phenomena and solve problems encountered in their ever-changing world' (ACARA, 2013). It highlights how chemistry relates to each and every thing that can be sensed, from the nanotechnology level to massive complex structures. Students are made aware of how issues such as sustainability, supply of clean drinking water, efficient production and use of energy, acidification of the oceans and climate require the application of chemical knowledge in developing solutions.

Chemistry is frequently called the 'central science' because it incorporates and connects the sciences of biology and physics and serves of great importance in engineering applications and medical fields. This book links chemistry to other disciplines of science by considering examples such as nanotechnology, energy, extraction of metals and production of sustainable materials.

The chemistry chapters explain the understanding and skills that are fundamental to a course of study in chemistry. They deal with how materials form, their composition and properties, how they change and the energy they consume or release through these changes. Theories and models that form the basis of chemical understanding and its use as a predictive tool in investigations and research are emphasised. The experimental nature of chemistry is modelled and students are provided with many opportunities to design and conduct their own experimental research in order to challenge their own understanding of this discipline.

The contextual, methodological approach is designed to ensure students can reach the highest possible standard. The intention has been to ensure all students achieve the level of depth and interest necessary to pursue tertiary studies in chemistry, engineering, technology and other scientific courses.

Each context and chemistry chapter follows a consistent pattern. Relevant learning outcomes from the Science Understanding and Science Inquiry Skills strands appear on the opening page of the chemistry chapters. Science as a Human Endeavour learning outcomes appear on the opening page of the context chapters.

Worked examples, written to connect important ideas and solution strategies, are included throughout the text. Solutions are written in full, including an explanation of the processes used to arrive at the solution. In order to consolidate learning, students are challenged to try similar questions on their own.

Numerous question sets appear at the end of major sections in the book and there is a comprehensive set of review questions at the end of each chapter. All questions have been graded from lower- to higher-order thinking skills: Remembering, Understanding, Applying, Analysing and Reflecting. Numerical answers appear at the end of the book and complete worked answers appear on the teacher website.

Experiments and Investigations demonstrate the high level of importance the authors attach to understanding-by-doing chemistry. These activities introduce, reinforce and enable students to practise Science Inquiry Skills, especially experimental design, data collection, analysis and conclusions. The Scientific Investigations chapter consolidates important investigative concepts and values. It enables students to learn and reflect on their experience as puzzle-solvers and investigators.
It is an invaluable tool for students undertaking an Extended Experimental Investigation.

Nelson Chemistry for the Australian Curriculum Units 3 & 4 provides students with a comprehensive study of chemistry that will fully prepare them for a range of different types of assessment and any future studies in the area.

Debra Smith

Series editor

AUTHOR AND REVIEWER TEAMS

Authors

Debra Smith
Debra Smith is an experienced Chemistry teacher and author. Debra has been Head of Science at a number of Queensland high schools and has developed Science curriculum material for Education Queensland schools. She has been President and Treasurer of the Australian Science Teachers' Association. Debra has been involved in writing science curriculum at the local, state and national levels. For her contribution to science education, Debra was awarded the 2010 Prime Minister's Prize for Excellence in Science Teaching in Secondary Schools.

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Rachel Whan
Rachel Whan studied Veterinary Science at the University of Queensland before completing a Graduate Diploma in Education at the University of Southern Queensland. Since then she has taught Chemistry, Biology, Human Biology, Science, Mathematics and Agriculture in a variety of schools in both Queensland and Western Australia including State, Catholic and Independent schools. She is currently teaching Chemistry, Human Biology and Science at St Brigid's College in Lesmurdie, WA, where she has been the PK–12 Team Leader for Science for the past 7 years. Rachel has been involved in the implementation of state, national and international curriculums across all year levels and has also been involved in the marking and moderation of Chemistry at a state level. Rachel was a co-author of the MYP Science for the International Student IB series of textbooks published by Cengage.

Reviewers

The publisher and authors would like to thank the reviewers for their valuable assistance in developing the manuscript.

- Paul Walker – Grace Christian School, WA
- Pat Corbin – Lutheran College, Qld
- Hayley Bridgewood – Wesley College, Vic
- Charles Coleiro – Ave Maria College, Vic

USING NELSON CHEMISTRY

Nelson Chemistry Units 3 & 4 for the Australian Curriculum provides a contextual approach to the teaching and learning of chemistry. Four relevant contexts have been provided as the first four chapters of the book. These contexts are specifically written to develop the understandings identified in the Science as a Human Endeavour strand. The contexts show how chemistry knowledge can be applied in real-world situations. The chemistry knowledge that links into these contexts has been provided as the next nine chapters. Students will find it easy to navigate between the context and the chemistry content chapters through the use of linking icons. Teachers also have the flexibility of providing their own contexts and still being able to use the chemistry chapters provided in this book.

Science Inquiry Skills have been integrated within the context and chemistry chapters so the students can see the interconnectedness between the theoretical and practical aspects of chemistry.

Each context begins with a concept map that shows the interrelationships between the context, the chemistry content and inquiries and activities. It links to the relevant content of the three strands of the senior Chemistry Australian Curriculum.



Each chapter and context begins with a **Chapter opener**. This page in chemistry chapters presents the Science Understanding content descriptions from the senior Chemistry Australian Curriculum. This page in the context chapters presents the Science as a Human Endeavour content descriptions.

The text has been authored and reviewed by experienced chemistry educators to enable students to achieve the maximum level of achievement of which they are capable. A number of devices have been utilised to improve literacy and understanding. One of these is the use of short sentences and paragraphs. This is coupled with clear and concise explanations and real-world examples. New terms are bolded as they are introduced and appear in an end-of-chapter and an end-of book glossary.

Important concept

Throughout the text, important ideas, formulas and laws are summarised in **Important concept** boxes.

WORKED EXAMPLE

Step-by-step instructions on how to perform chemical calculations are shown in the **Worked examples**. The logic behind each step is explained. Students are then able to practise these steps by attempting the related problems presented at the end of the worked example.

Chemistry is a practical subject and students need to be given the opportunity to explore and discover through inquiry, which includes practical and research activities. These are presented in three different types of boxes throughout the text.

ACTIVITY

The **Activities** provide the opportunity for short, hands-on tasks to clarify or reinforce a concept. The activities can be performed either individually or in groups.

INVESTIGATION

The **Investigations** allow students to develop, practise and reinforce Science Inquiry Skills. They provide students with the opportunity to design and carry out their own scientific investigation either individually or in a group. Students are prompted to consider ideas for improvement and further investigation to illustrate that investigating involves an ongoing and improving process. Further information on how to conduct a scientific investigation can be found in the Scientific Investigations chapter on page 455.

EXPERIMENT

The **Experiments** reinforce the Science Inquiry Skills strand of the Australian Curriculum. Experiments contain guided instruction on the materials, procedure, collection and analysis of results and discussion.

Risk assessment

The **Risk assessment** table occurs within experiments and investigations. The table highlights the risks to the students and provides suggestions on how to minimise these risks. Teachers are able to supplement this table by adding any further risks specific to the school situation. It also provides a scaffold so that students can begin to conduct their own risk assessments.

Links between Context chapters and Chemistry chapters occur via the **Linking boxes**. One context chapter may be linked to several chemistry chapters, and a chemical concept may be linked to a number of contexts demonstrating application of the same chemistry knowledge in different situations.

At times it is necessary to add an extra piece of information, a curriculum link or an encouraging note. This is done using **Margin notes**.

Margin note

The Chemistry curriculum draws on knowledge and understanding from across Biology, Earth and Environmental Science, Mathematics and Physics. Knowledge from these areas also provides students with an enriched understanding of chemistry.

Review of student understanding is attained through the **Question sets** throughout the chemistry chapters. Questions are ordered from lower- to higher-order thinking skills. The addition of Reflection questions gives students the opportunity to reflect upon not only what they are learning but why and how they are learning it.

QUESTION SET



The end-of-chapter review provides:

- a **Summary** or **Checklist** of the important concepts presented within the chapter. This will be a valuable tool when students are revising for tests and exams
- a **Glossary** of all the new terms introduced within the chapter
- **Chapter review questions** (in Chemistry chapters) that review understanding of concepts from the chapter. Questions are ordered from lower- to higher-order thinking skills and include Reflection questions.

Where answers to questions are numerical, they are provided in the back of the book.



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CURRICULUM GRID

		Context						Chemistry										
		1	2	3	4	5	6	1	2	3	4	5	6	7	8	9	10	11
Science as a Human Endeavour	ICT and other technologies have dramatically increased the size, accuracy and geographic and temporal scope of data sets with which scientists work (ACSCH082 AND ACSCH120)	✓			✓													
	Models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory power (ACSCH083 AND ACSCH121)			✓	✓													
	The acceptance of scientific knowledge can be influenced by the social, economic, and cultural context in which it is considered (ACSCH084 AND ACSCH122)						✓											
	People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk (ACSCH085 AND ACSCH123)		✓				✓											
	Science can be limited in its ability to provide definitive answers to public debate; there may be insufficient reliable data available, or interpretation of the data may be open to question (ACSCH086 AND ACSCH124)		✓		✓													
	International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia-Pacific region (ACSCH087 AND ACSCH125)		✓	✓	✓	✓												
	Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCH088 AND ACSCH126)	✓	✓	✓	✓	✓	✓											
Science Inquiry Skills	Identify, research, construct and refine questions for investigation; propose hypotheses; and predict possible outcomes (ACSCH074 AND ACSCH112)			✓	✓	✓		✓		✓	✓	✓		✓		✓		✓
	Design investigations, including the procedure/s to be followed, the materials required, and the type and amount of primary and/or secondary data to be collected; conduct risk assessments; and consider research ethics (ACSCH075 AND ACSCH113)	✓		✓	✓	✓		✓	✓	✓	✓	✓	✓	✓		✓		✓
	Conduct investigations, including: – using volumetric analysis techniques and constructing electrochemical cells, safely, competently and methodically for the collection of valid and reliable data (ACSCH076) – including using organic synthesis methods and collating data from chemical analyses, safely, competently and methodically for the collection of valid and reliable data (ACSCH114)				✓	✓				✓	✓	✓	✓	✓				✓ ✓

		Context						Chemistry										
		1	2	3	4	5	6	1	2	3	4	5	6	7	8	9	10	11
	Represent data in meaningful and useful ways, including using appropriate graphic representations and correct units and symbols; organise, process and analyse data to identify trends, patterns and relationships; identify and distinguish between random and systematic errors, and estimate their effect on measured results; discuss how the nature of the procedure and the sample size may influence uncertainty and limitations in data; and select, synthesise and use evidence to make and justify conclusions (ACSCH077 AND ACSCH115)	✓		✓		✓				✓	✓	✓	✓	✓	✓	✓		✓
	Interpret a range of scientific texts, and evaluate processes, claims and conclusions by considering the quality of available evidence, including confidence intervals in secondary data; and use reasoning to construct scientific arguments (ACSCH078) Interpret a range of scientific and media texts, and evaluate processes, claims and conclusions by considering the quality of available evidence; and use reasoning to construct scientific arguments (ACSCH116)	✓		✓	✓					✓	✓				✓			
	Select, construct and use appropriate representations, including: – half-equations, balanced chemical equations, equilibrium constants and expressions, pH, oxidation numbers, standard electrode potentials and cell diagrams, to communicate conceptual understanding, solve problems and make predictions (ACSCH079) – physical, virtual and graphical models of primary, secondary and tertiary structures, structural formulas, chemical equations, systematic nomenclature (using IUPAC conventions) and spectra, to communicate conceptual understanding, solve problems and make predictions (ACSCH117)	✓		✓	✓			✓	✓	✓	✓	✓	✓	✓	✓		✓	
	Select and use appropriate mathematical representations to solve problems and make predictions, including: – calculating cell potentials under standard conditions, using the mole concept to calculate moles, mass, volume and concentrations from volumetric analysis data, determining the yield of incomplete reactions, and calculating the pH of solutions of strong acids and bases (ACSCH080) – using the mole concept to calculate quantities in chemical reactions, including multi-step reactions, and the percentage yield of synthesis reactions (ACSCH118)	✓							✓		✓	✓			✓	✓		
	Communicate to specific audiences and for specific purposes using appropriate language, nomenclature, genres and modes, including scientific reports (ACSCH081 AND ACSCH119)				✓	✓			✓	✓	✓		✓	✓	✓			✓

CONTEXT 1
WINE



Shutterstock.com/Timothy Hodgkinson

By the end of this chapter you will have covered the following material.

Science as a Human Endeavour

- ICT and other technologies have dramatically increased the size accuracy and temporal scope of data sets with which scientists work (ACSCH082 and ACSCH120)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environment impacts and to design action for sustainability (ACSCH088 and ACSCH126)

Contextual story – Wine

- Wine: composition and control
- The history of wine
- The wine industry today
- Fermentation: making alcohol
- Sugar content
- Acids in wine
- The wine matrix
- Maintaining the balance
- Making wine: white versus red
- Alcohol in the blood
- Greening the wine industry

Chemical Understanding

- The importance of the pH scale
- Acidity constants
- Polyprotic acids: K_a
- Buffers
- Analytical techniques: faster and better
- Mass spectroscopy
- NMR
- IR spectroscopy
- UV–visible spectroscopy
- Volumetric analysis (titrations)
- Controlling equilibrium
- Oxidation and reduction
- Alcohols, carboxylic acids, esters, aromatics, aldehydes
- Carbohydrates

Investigations

Context 1

- Activity 1.1 Balancing the sugars
- Activity 1.2 Sour lollies
- Activity 1.3 Buffer capacity of wine
- Activity 1.4 Esters in wine
- Activity 1.5 Redox phenomena in wine
- Activity 1.6 Sustainability in the wine industry
- Investigation 1.1 Alcohols in alcoholic drinks

Chapter 4

- Experiment 4.6 Measuring the concentration of alcohol by titration
- Experiment 4.7 Determination of sulfur dioxide content of wine

Science as a Human Endeavour (SHE)

- ICT and other technologies have dramatically increased the size accuracy and temporal scope of data sets with which scientists work (ACSCH082 and ACSCH120)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCH088 and ACSCH126)

Science Understanding (SU)

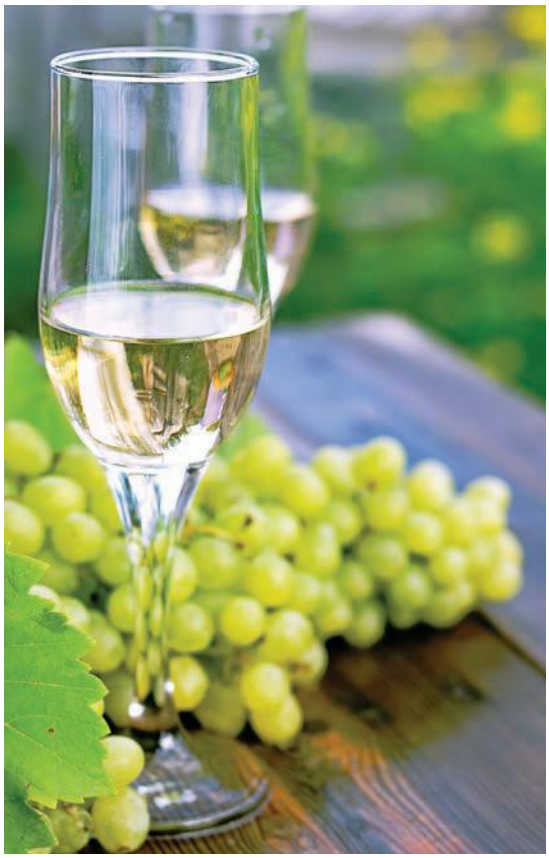
- Over time, physical changes and reversible chemical reactions reach a state of dynamic equilibrium in a closed system, with the relative concentrations of products and reactants defining the position of equilibrium (ACSCH091)
- The effect of changes of temperature, concentration of chemicals and pressure on equilibrium systems can be predicted using Le Chatelier's principle (ACSCH095)
- Acids are substances that can act as proton (hydrogen ion) donors and can be classified as monoprotic or polyprotic depending on the number of protons donated by each molecule of the acid (ACSCH097)
- The strength of acids is explained by the degree of ionisation at equilibrium in aqueous solution, which can be represented with chemical equations and equilibrium constants (K_a) (ACSCH098)
- The relationship between acids and bases in equilibrium systems can be explained using the Brønsted–Lowry model and represented using chemical equations that illustrate the transfer of hydrogen ions (ACSCH099)
- The pH scale is a logarithmic scale and the pH of a solution can be calculated from the concentration of hydrogen ions; K_w can be used to calculate the concentration of hydrogen ions from the concentration of hydroxide ions in a solution (ACSCH100)
- Acid–base indicators are weak acids or bases where the acidic form is of a different colour to the basic form (ACSCH101)
- A range of reactions, including displacement reactions of metals, combustion, corrosion and electrochemical processes, can be modelled as redox reactions involving oxidation of one substance and reduction of another substance (ACSCH103)
- Organic molecules have a hydrocarbon skeleton and can contain functional groups, including alcohols, carboxylic acids, esters, amines and amides (ACSCH127)
- Each class of organic compounds displays characteristic chemical properties and undergoes specific reactions based on the functional groups present; these reactions, including acid–base and oxidation reactions, can be used to identify the class of organic compound (ACSCH128)
- Data from analytical techniques, including mass spectrometry, X-ray crystallography and infrared spectroscopy, can be used to determine the structure of organic molecules, often using evidence from more than one technique (ACSCH130)

Science Inquiry Skills (SIS)

- Design investigations, including the procedure/s to be followed, the materials required, and the type and amount of primary and/or secondary data to be collected; conduct risk assessments (ACSCH075)
- Select, construct and use appropriate representations, including equilibrium constants, expressions and pH, to communicate conceptual understanding, solve problems and make predictions (ACSCH079)
- Select and use appropriate mathematical representations to solve problems and make predictions, including calculating using the mole concept to calculate moles, mass, volume and concentrations from volumetric analysis data and calculating the pH of solutions of strong acids and bases (ACSCH080)
- Communicate to specific audiences and for specific purposes using appropriate language, nomenclature, including scientific reports (ACSCH081)
- Represent data in meaningful and useful ways, including using appropriate graphic representations and correct units and symbols, organise and analyse data to identify patterns and relationships; synthesise and use evidence from a range of sources to make and justify conclusions (ACSCH115)
- Interpret a range of scientific and media texts, and evaluate processes, claims and conclusions by considering the quality of available evidence; and use reasoning to construct scientific arguments (ACSCH116)
- Select, construct and use appropriate representations, including structural formulas, chemical equations, systematic nomenclature (using IUPAC conventions) and spectra, to communicate conceptual understanding, solve problems and make predictions (ACSCH117)
- Select and use appropriate mathematical representations to solve problems and make predictions (ACSCH118)

Wine – composition and control

Wine is an alcoholic drink, produced from the fermentation of grapes or grape juice. The word 'wine' originates from the Latin *vinum*, which means both wine and vine. Ethanol is the main alcohol in wine, but wine is much more than a solution of ethanol. The quality of wine is influenced by the soil, climate, type of grapes and the agricultural and wine-making processes used. The production of wine relies on controlling reversible reactions that balance acidity, alcohol concentration, sugar levels and the colour of the wine.



Ortodox/Shutterstock.com

▲ **Figure 1.1**
A glass of wine is more than a solution of ethanol.

History of wine

The history of wine predates recorded history. Archaeologists have evidence that wine was being produced in India 2000 years ago, in Greece and China 6500 years ago and by the Egyptians and Iranians 7000–8000 years ago.

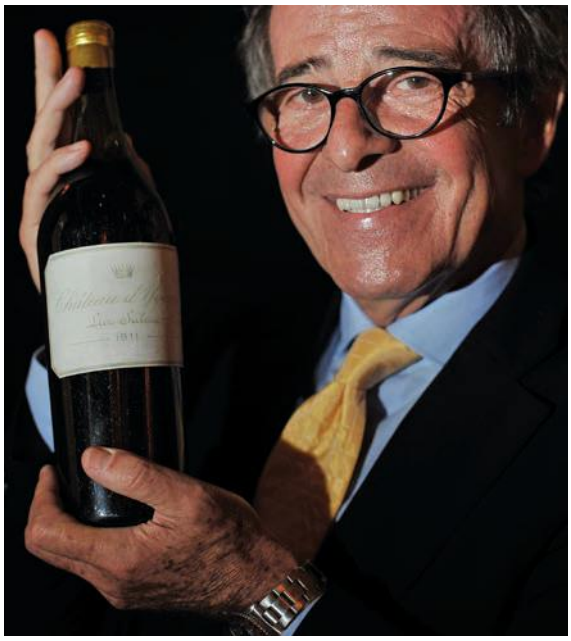
Australian production of wine started with the First Fleet of 1788. Governor Phillip brought vines from Rio de Janeiro in Brazil and the Cape of Good Hope, South Africa, and planted them in Farm Cove, the current site of the The Royal Botanic Garden, Sydney. However, these vines never managed to produce wine or grapes. By 1822 wine was being exported back to Europe. The production and quality of Australian wine was improved by the knowledge and skills of the emigrants from around the world. This included Prussian emigrants in the mid-1850s who established Australia's premier wine region, the Barossa Valley in South Australia.

WOW

Expensive wine!

The most expensive wine ever sold were bottles of Champagne from the 1907 vintage from the Heidsieck vineyard in France. Originally intended for the doomed Russian Imperial family in 1916, the bottles were lost in a shipwreck off the coast of Finland. In 1997, more than 200 bottles were found by divers and were later sold for $275 000.

A single bottle of sweet white wine was sold in 2011 for an impressive $120 000 to wine collector Christian Vanneque. The wine was a Château d'Yquem from the Bordeaux region in France and was produced in 1811, the year the comet Flaugergues was visible. Some winemakers and enthusiasts, somewhat superstitiously, attribute good characteristics to wine in the years where comets are visible from Earth. Christian Vanneque plans to drink the wine in August 2017.



BEN STANSALL/AFP/Getty Images

▲ **Figure 1.2**
Christian Vanneque with the 1811 Château d'Yquem bottle he bought for $120 000



To learn about the group of compounds called alcohol, such as ethanol and its properties, refer to Chemistry section 6.6, page 298.

The wine industry today

In just 200 years, the Australian wine industry has grown to be worth approximately $2.8 billion domestically and exports approximately 750 million litres of wine a year. The wine industry provides jobs for scientists in **viniculture** (the science of growing the vine) and **oenology** (wine production). There are also additional jobs connected to the wine industry, such as those involved in tourism to the wineries and exporting the wines.

Australians consume around 530 million litres of wine annually, approximately 30 litres for each adult. Wine is produced in every state in more than 60 wine regions, the majority being in the southern cooler areas of the country. Each region has its own climate and soil type and produces a different variety and style of wine. The wine can be generally classed as red or white based upon the colour of the grapes used. Wine can be further separated into varieties according to the type of grapes.

The main varieties produced in Australia are Shiraz, Cabernet Sauvignon, Chardonnay, Merlot, Semillon, Pinot Noir, Riesling and Sauvignon Blanc. The skilled **oenologist** (wine maker) knows how to blend the grapes and to control the processing and fermenting of the grapes to produce a quality wine with desired characteristics. Each variety will differ in colour, taste and texture. The taste and quality of the wine are also influenced by how long the wine is **aged**.

ICT and other technologies have dramatically increased the size, accuracy and temporal scope of data sets with which scientists work. (ACSCH082 and ACSCH120) AC

WOW

What's in a name?

Champagne wine undergoes a difficult and expensive second fermentation in the bottle in a process called *méthode champenoise*. It is a variety that is produced only in the Champagne region of France. The name 'Champagne' is restricted to wines made in the Champagne region and by the *méthode champenoise*. By law, other wines produced from the same grapes and by the same method are called 'sparkling wines'. Protecting the name was considered so important that this restriction was included in the Treaty of Versailles after World War I.

Technology in the wine industry

ICT and other technologies are playing an important role in this large industry. The use of analytical instruments in the wine industry allows scientists to learn more about the complex chemistry of wine and to discover the chemical pathways of some of the key molecules in wine.

Since 1971, the Australian Wine Research Institute has been undertaking research using mass spectroscopy. Mass spectroscopy combined with chromatography can detect pesticides, identify toxins and help determine the mechanisms involved in stabilising the colour of wine. Mass spectroscopy is used to produce certificates of quality for exporting wine as it can verify that the concentrations of pesticides, heavy metals and toxins are within the legal limits. This technique has also been used to detect illegal adulterations and test the claims of wine producers. This helps protect the consumer's health.

Other instruments are also used. Nuclear magnetic resonance (NMR) spectroscopy can determine whether wine is 'spoilt' (vinegary) without opening the bottle. NMR spectroscopy is also used to authenticate wine and to detect changes in chemical composition. In May 2013, researchers in Germany developed a technique using ^{1}H (proton) NMR spectroscopy to authenticate the grape variety, the geographical origin and the vintage (the year it was produced) of a wine. They used the NMR spectrum as the individual 'fingerprint' of a wine sample. This provided a wealth of information about the variety, origin, vintage and even how the wine has been treated. This not only provides information to the winemakers and scientists but it can also be used in cases of fraud.



To learn more about the instrumental techniques of mass spectrometry and NMR spectroscopy, refer to Chemistry section 8.4, page 384.



RESEARCHING WINE

Visit this website to learn more about the instruments and testing that are used in wine making.

WOW

Trailblazing wine cask

The wine cask is an Australian invention. In the 1960s, Tom Angrove from Angrove Wines was trying to work out how to sell wine in bulk. Large bottles once opened let in air, which can spoil the wine in a couple of days. The first wine cask was a 4-litre soft plastic bag inside a cardboard box. When the bag was opened, the corner could be pegged off to protect the wine. Penfold Wines then developed a plastic, airless flow tap connected to a metallised plastic bag. The wine can be tapped, mimicking the more traditional oak casks.

Grapes versus wine

Wine is made from the **fermentation** of grapes. Yeast in the absence of oxygen converts the grape sugars into alcohol. The main difference between wine and grape juice is the level of these two components (Table 1.1). Each variety of wine will have slight differences in composition: some varieties are sweeter, others are considered 'lighter' as they have lower **tannin** levels.

The minor components present in wine are responsible for some of the subtle flavours and colour of the wine. The skill of the winemaker is in controlling the level and maintaining the required chemical balance within the wine. The four main factors that have to be balanced are the acidity, alcohol, sugar levels and the colour of the wine.

Table 1.1 Quantities of some components of typical wine and grape juice

Component	Typical wine % composition	Typical grape % composition
Water	85–89	74–78
Sugar	0–8	18–25
Alcohol (ethanol)	10–14	0.0
Acids	0.5–0.8	1.0
Tannin	<0.1	0.2
Other (salts, proteins)	<0.1	0.1

The acids in wine are generally carboxylic acids. Other compounds in wine are aldehydes formed from the oxidation of alcohols and esters formed the reaction of alcohols and carboxylic acids.



To learn more about the structure and reactions of the different groups of organic molecules (alcohols, aldehydes, carboxylic acids and esters), refer to Chemistry sections 6.5–6.9, pages 296–314.

Fermentation – making alcohol

Historically, grapes were fermented by a 'wild' type of yeast found on grape skin. Yeast turns sugars such as glucose ($C_6H_{12}O_6$) into ethanol and carbon dioxide, when no oxygen is present. This in an anaerobic reaction:

$$C_6H_{12}O_6(aq) \rightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$$

The alcohol content of wine is due to the amount of sugar present in the grapes and the success of the fermentation process. Generally, the higher the sugar content of the grape, the higher the alcohol content of the wine. The winemaker may stop fermentation early to leave some sugar unreacted and to make a sweeter wine.

Fermentation is an exothermic process. In winemaking, the temperature cannot exceed 29°C for red wines or 18°C for white wines. Above these temperatures, enzymes involved may be denatured and the fermentation will stop. Lower temperatures are desirable because this limits the loss of volatile aromas and flavours. Yeast is naturally killed when the ethanol content reaches around 14% v/v. Wild yeast can cause the fermentation to stop prematurely, leaving a high sugar content in the wine, so more predictable commercial yeasts are used.

Measuring the alcohol level

The winemaker will monitor the production of alcohol during fermentation as part of quality control. It is a legal requirement that the final alcohol level be measured and reported on the bottle's label. There are various ways to determine the alcohol level, including by monitoring density changes and titration.

As fermentation proceeds, the density of the mixture decreases. This is due to ethanol's lower density (0.789 g mL^{-1} at 25°) compared to that of water (1 g mL^{-1}). A hydrometer is one way of tracking the change in density.

A titration, or more specifically a back titration, can be used to measure the alcohol content of wine. Back titration techniques are used when the reaction is too slow for a direct titration or no suitable indicator is available for the direct reaction. This back titration uses redox reactions.



To learn more about back titrations, refer to Chemistry section 4.5, page 238. For titrations using redox reactions, refer to Chemistry section 4.5, page 243.

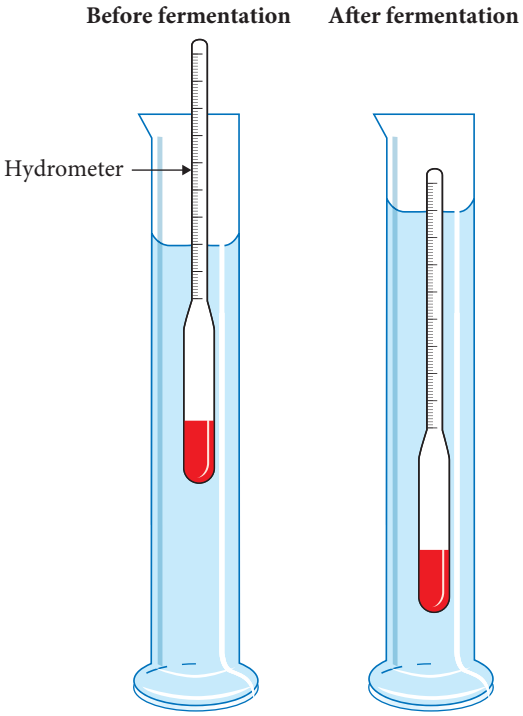


Figure 1.3 ▶ The hydrometer is used to monitor the fermentation process. The hydrometer will 'float high' at the start of fermentation (left). As alcohol is produced and the density falls, the hydrometer will sink.



Cultura Creative (RF)/Alamy

Figure 1.4 ▶ Students undertaking a titration experiment



To learn more how infrared spectroscopy can be used to measure the alcohol content of wine, refer to Chemistry section 8.5, page 392.



METHANOL

Visit this website to learn more about the health effects and treatments for consuming methanol in alcoholic drinks.

Gas chromatography (GC) can detect the amount of ethanol and other alcohols such as methanol, which is naturally produced in the fermentation process in small quantities. Methanol is highly toxic. It can be fatal or cause permanent brain damage at quite low doses. Methanol must be present at less than $2\,g\,L^{-1}$ of ethanol content for white wine and less than $3\,g\,L^{-1}$ of ethanol in red wine. Higher levels in wine usually indicate that illegal tampering or adulteration of the wine has occurred.

The wine industry also uses infrared spectroscopy. A near-infrared spectrometer measures the alcohol content quicker and more reliably to produce better-quality wines. A specific range is used so that the other constituents of the wine do not influence the result. This means the one procedure can work for white or red wine, sweet or dry wine.

INVESTIGATION 1.1

ALCOHOLS IN ALCOHOLIC DRINKS

More than one alcohol is produced when grapes are fermented. Alcoholic drinks produced from the fermentation of different foods, such as grain, also produce different alcohols. When fermented drinks are distilled to make spirits, the proportions of these alcohols change. Making wine at home is legal, but it is illegal to distill without a licence.

In Australia, people have been killed or seriously injured when they unknowingly consumed these alcohols in homemade or adulterated drinks. Understanding which alcohols are present in drinks and how the drinks have been produced is important to health experts and law enforcers.

Aim

To explore the different alcohols present in alcoholic drinks and how instruments can be used to determine how the alcoholic drink was produced

What will you need?

- Computer with internet access

How will you carry out your investigation?

1 Research wood alcohol and 'fusel oil'.

2 Research the difference in production for the clear alcohols vodka and gin compared to brandy and cognac.

What results will you collect?

1 Draw the structures for each of the following molecules that are typically found in wine.

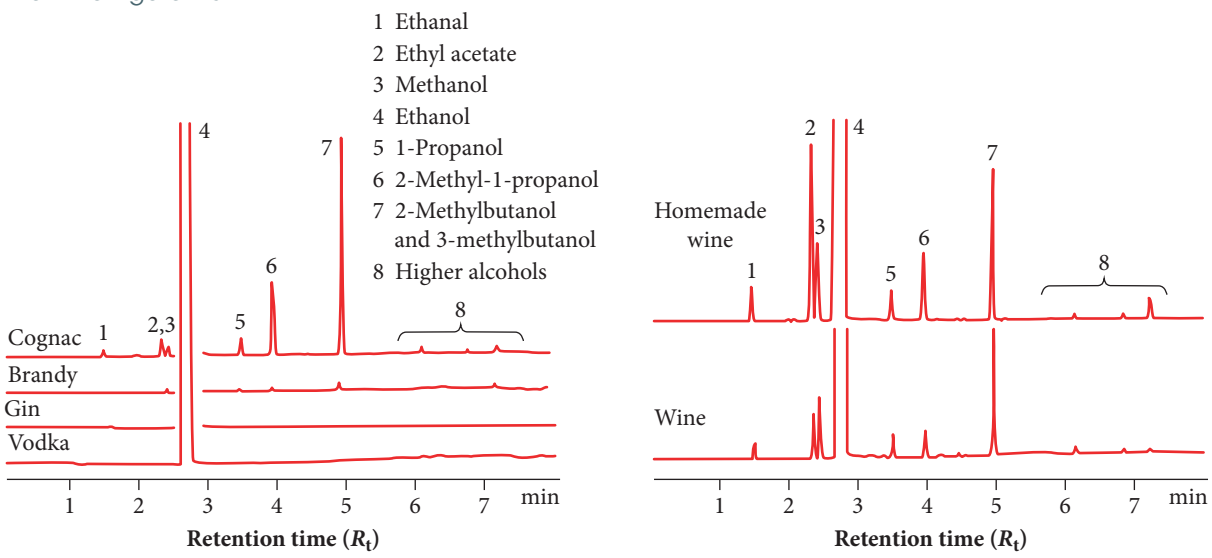
- **a** Ethanol
- **b** Ethanal
- **c** Ethyl ethanoate
- **d** Hexanol, higher alcohols
- **e** 2-Methyl-1-propanol
- **f** 2-Methylbutanol
- **g** 3-Methylbutanol
- **h** 1-Propanol
- **i** Methanol

2 Classify the molecules in Question **1** as alcohols, esters or aldehydes.

3 Briefly explain the differences between vodka, gin, wine, brandy and cognac.

How will you analyse your results?

1 Examine Figure 1.5.



▲ **Figure 1.5** Gas chromatograms for six different alcoholic drinks: vodka, gin, brandy, cognac, a commercial wine and a homemade wine

2 Copy and complete the following table by referring to Figure 1.5 and listing the main components in wine according to their retention time R_t.

Wine component	Retention time (R_t)
	1.5
	2.3
	2.5
	2.8
	3.5
	3.9
	5.1
	6–7.5

3 Gas chromatography separates molecules by their molecular weights and volatility. Explain the order of the components.

What have you found?

1 Describe the alcohols present in wine and other alcoholic drinks.

2 Describe the differences observed in the different alcoholic drinks.

What do you conclude?

Comment on how the use of techniques such as gas chromatography can determine how a substance was produced.

Ideas for improvement or further investigation

Research the connection between the higher alcohols and hangovers.

Taking it further

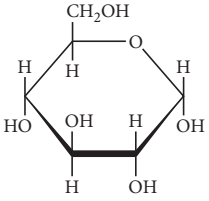
Explain why methanol is much more toxic than ethanol. How are these alcohols treated in the body?

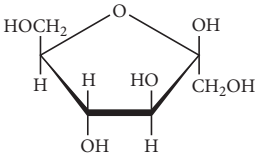
Sugar content of wine

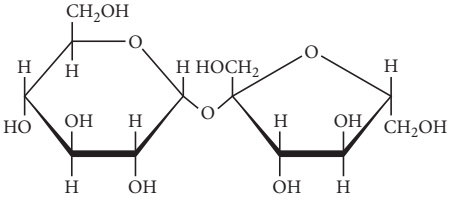
Grape variety, how the vine is treated and the environmental conditions all alter the sugars present in grapes. These factors have to be controlled to achieve the required balance of alcohol and sugar after fermentation. There has to be enough sugar present in grapes for fermentation to occur. The type of sugar present is also important.

The three main sugars in grapes are sucrose, fructose and glucose. The proportions of the three sugars change as grapes ripen. At the start, sucrose is the main sugar present and the young berries have more glucose than fructose. As the grapes ripen, the percentage of sucrose decreases and the percentage of the other sugars increase up to 25 per cent. When fully ripened, there is more fructose than glucose. Fruits are sweetest when fully ripe due to the sweetness of fructose.

▼ **Figure 1.6**
Glucose, fructose and sucrose are the three main sugars in wine.









foodfolio/Alamy

Glucose



Richard Warburton/Alamy

Fructose



sss615/Shutterstock.com

Sucrose

When the total sugar levels are too high, there is a risk that the yeast will be killed due to the resultant high alcohol levels. Most commercial yeasts are **glucophilic** and will consume glucose in preference to fructose. If fermentation stops, as fructose is the most common sugar left, it is difficult to restart. For these reasons, no wine is ever fermented completely.

The sugar remaining in the wine when fermentation stops is called **residual sugar**. Small amounts of other sugars, such as other pentoses, are present in the grapes. These sugars are not fermentable so are present at the end in the wine as residual sugars. The amount of sugar in wine is another way of classifying wine. Wines can range from dry or sweet. In dry wines, most of the sugar is converted into ethanol and so the residual sugar amount is less than $4\,g\,L^{-1}$. In sweet wine, not all the sugar is converted into ethanol, so the residual sugar is more than $45\,g\,L^{-1}$.

Measuring the sugars

Chemists use many instruments to determine which sugars are present in wine. Chromatography methods such as high-performance liquid chromatography and gas chromatography can separate the different sugar components. Mass spectroscopy and NMR techniques can help to identify the different sugars and their relative abundance and how the composition changes over time.



To revise information about sugars, carbohydrates and the structure of these molecules, refer to Chemistry section 7.5, page 349.

ACTIVITY 1.1

BALANCING THE SUGARS

Aim

To investigate the sugars used in the manufacturing of lollies

You will need

- Computer with internet access

What to do

1. Use Figure 1.6 to write the molecular formulas for glucose, fructose and sucrose.
2. Research:
   a. when these sugars are used in the manufacturing of lollies.
   b. why different sugars are used.
3. Research a method to make an 'inverted syrup'.

What did you discover?

1. What properties are enhanced by the different sugars?
2. What are inverted sugars?
3. Why are inverted sugars used when making lollies?
4. How easy is it to make **inverted sugar**?
5. What are the roles of the other ingredients needed to make inverted sugar?
6. Could you taste the difference between these sugars?



To revise and learn more about pH, see Chemistry section 2.2, page 180.



To learn more about carboxylic acids refer to Chemistry section 6.8, page 307.

Acids in wine

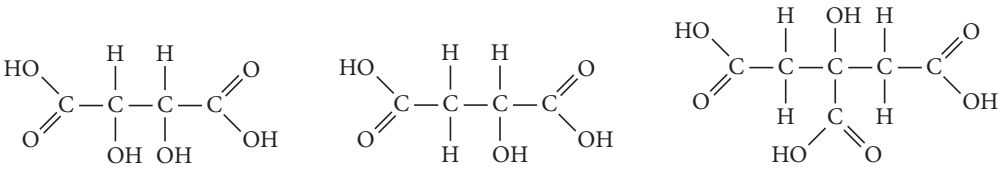
The acidity of wine is one of the main factors that contribute to its taste. Acidity balances residual sugar and alcohol. A wine high in sugar will not taste sickly sweet if it is balanced with a high acid level. Low acidity (high pH) reduces the amount of subtle flavours in the grapes and wine. Grapes grown in excessively warm climates are often too sweet. This is why most of the wine regions are in cooler climates.

The pH of the fermentation mixture is also important as the enzymes in yeast have an optimum pH. The acid level in wine also helps the microbial action of SO_2 (the main preservative); it helps desirable microorganisms and enhances the wine's colour and flavour.

There are more than 40 organic acids found in wine. These organic acids are weak acids. Weak acids have the general symbol HA. Weak acids only partially ionise in water to form hydronium ions and the anion A^-. The acids may be present as salts. The most common acids are tartaric acid, malic acid and citric acid; ascorbic acid, amino acids and phenolic acids are found in much smaller concentrations. These acids are present in the grapes.

For monoprotic acids such as lactic acid, the general symbol is HL. The diprotic acids malic and tartaric have the general symbol H_2M and H_2T, respectively. Tartaric acid is present as H_2T or the salts KHT (potassium hydrogen tartrate) and K_2T (dipotassium tartrate). Tartaric acid makes the greatest contribution to the pH of wine. Citric acid has the general symbol H_3C as it is a triprotic acid.

Malic acid accumulates in the berries before they ripen. Through the ripening process, the amount of malic acid decreases as it is broken down to different sugars. The concentration of malic acid is used to judge when the fruit is ripe. Malic acid confers a tart taste to wine.



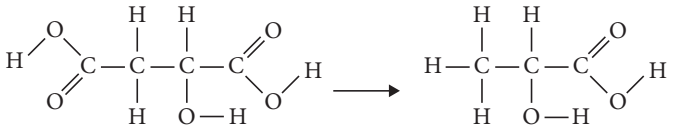
◀ **Figure 1.7**
The most common acids in wine



To learn about the weak acids, ionisation, polyprotic acids and K_a, refer to Chemistry sections 2.3–2.5, pages 181, 188 and 194.

Other acids in wine are by-products of the fermentation process. The one acid the wine makers try to avoid is acetic acid (ethanoic acid). If oxygen gets into wine, the oxidation reaction of ethanol to ethanoic acid occurs and the wine can turn into vinegar – the wine is 'spoilt'. Spoilt wine can be made into red or white wine vinegars.

After fermentation, the wine is settled. Settling allows the particles of skin and pulp to precipitate. Yeast cells break down within the precipitate, stimulating the growth of bacteria that convert malic acid into lactic acid. Lactic acid causes the wine's taste to mellow. Examine the structures and the K_a values of the two acids lactic acid and malic acid in Figure 1.8 to see why. This second fermentation, called **malolactic fermentation**, is an optional process that the winemaker may use to reduce the acidity of the wine by organic rather than chemical means. It is typically used in red wines.



◀ **Figure 1.8**
Malic acid is converted to lactic acid during malolactic fermentation.

The acidity level of wine is also influenced by phenolic compounds. **Phenolics** provide the colour and **astringency** of the wine. They are responsible for the red in autumn leaves. The wine's **aroma** is influenced by the amino acids present and the taste and colour are influenced by the presence of phenol–carbonic acids.

Table 1.2 Common acids found in wine. The acids found in the grapes remain through the process and so are also found in wine. Others are added in the process or are by-products in the production of wine

Acid	Notes	Acids in grapes	Acids in wine
Tartrates H_2T (tartaric acid) KHT (potassium hydrogen tartrate) K_2T (dipotassium tartrate)	Occur naturally in grapes; biosynthesis unclear Added during winemaking	✓	✓
Malic acid H_2M	Occurs naturally in grapes; is converted into lactic acid after fermentation	✓	✓
Citric acid H_3C	Occurs naturally at a very low level	✓	✓
Lactic acid HL	Arises due to conversion from malic acid, post fermentation		✓
Acetic acid HA (ethanoic acid)	Produced by all yeasts and some bacteria		✓
Succinic, pyruvic acids	Small amounts during alcoholic fermentation		✓
Ascorbic acid (vitamin C)	Added as an antioxidant		✓
Carbonic acids	Produced by CO_2 reacting with water		✓
Sulfurous acid	Produced from added SO_2 reacting with water (food additive 220 or 202)		✓

ACTIVITY 1.2

SOUR LOLLIES

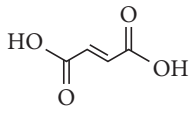
Aim

To investigate the structures and properties of citric, malic, tartaric and fumaric acids by investigating the formulations of sour lollies

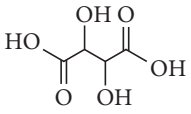
Fruit contains organic acids. These balance the sweetness of the sugar. These same acids are added to lollies. Each acid will affect the flavour, the physical properties and the intensity of sourness of the lollies.

Table 1.3 Common acids found in fruits

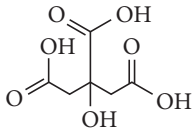
Fruit	Predominant acid	Secondary acid
Apple	Malic acid (95% of total acid)	Tartaric acid, fumaric acid
Apricot	Malic acid (70% of total acid)	Citric acid, tartaric acid
Lime, lemon	Citric acid	Malic acid
Mango	Citric acid	Malic acid, tartaric acid



Fumaric acid $K_{a1} = 8.85 \times 10^{-4}$, $K_{a2} = 3.21 \times 10^{-5}$



Tartaric acid $K_{a1} = 9.2 \times 10^{-4}$, $K_{a2} = 4.31 \times 10^{-5}$



Citric acid $K_{a1} = 7.45 \times 10^{-4}$, $K_{a2} = 1.73 \times 10^{-5}$, $K_{a3} = 4.02 \times 10^{-7}$

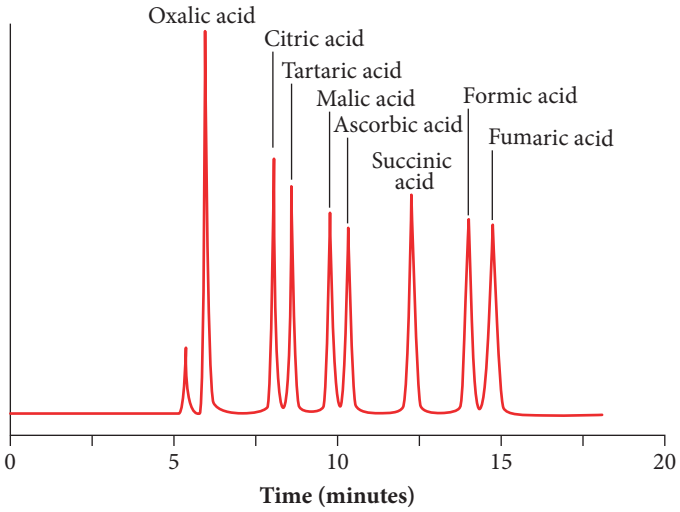
▲ Figure 1.9

You will need

- Computer with internet access

What to do

1. Research the organic acids in Table 1.3.
2. Examine the structures of citric, malic, fumaric and tartaric acids to see why these acids have a different intensity of acidity.
   - **a** What features show that the structures are organic?
   - **b** What structures form acids in water?
   - **c** Write the equations for each ionisation reaction.
   - **d** Which of these acids is the strongest?
   - **e** Acids can be classified as monoprotic, diprotic or polyprotic. Show by the use of equations what these terms mean and which one can be applied to each of these acids.
   - **f** What instrumental technique would you use to separate the acids?
   - **g** What instrumental techniques could have been used to identify the organic acids?
   - **h** What technique was used to produce Figure 1.10? Suggest an explanation for the order of the acids observed.



◀ **Figure 1.10**
Separation of organic acids found in fruit

2 In your group, decide which properties would be appropriate to investigate for manufacturing lollies. Then copy and complete the table below.

Solubility has been done for you.

Acid	Solubility in water at 20°C (%)	Hygroscopicity (ability to absorb moisture)		
Citric	62			
Fumaric	0.5			
Malic	56			
Tartaric	65			

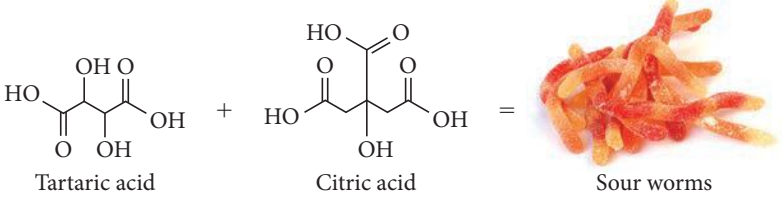
What did you discover?

1 Propose a reason why malic acid is commonly used in confectionary.

2 Why is fumaric acid used on the surface of sour lollies?

3 Which acid has the longest lasting acidic sensation? Which has a quick sour sensation?

4 Find a recipe for making sour lollies. Make the lollies and alter the acid used. Which acid is more effective?



padu_photo/Shutterstock.com

◀ **Figure 1.11**
Acids affect flavour, physical properties and sourness of lollies.

5 Design an experiment to test the claim that malic, fumaric and tartaric acids are perceived to taste more sour than an equal mass of citric acid.

6 Use the above information and your research to suggest why acidity of wine is usually reported as total acidity values, measuring tartaric acid and not individual acids.

Acidity levels

Controlling acidity is vital in the wine industry. Wine's pH depends on the total amount of acids present, the ratio of malic to tartaric acid and the amount of potassium present. The pH of a wine is fundamental to winemaking as it influences the colour, oxidation and biological and chemical stability of the wine. The pH of wine is in the range 2.9–4.2. Lower pH values are known to improve the stability, so winemakers usually prefer a pH range of 3.0–3.5. Winemakers use pH meters to measure the pH of the wine.

Titratable acidity



To measure the titratable acidity of a wine, refer to Chemistry section 4.5, page 238.

The amount of acid present is measured by titration. In the wine industry, it is called the **titratable acidity**. Titration acidity consists of acids that can be titrated by a strong base solution by reaction with their free carboxylic acid groups (–COOH). Some wine acids have carboxylic groups totally or partially neutralised by cations (potassium, sodium and/or calcium). If wine is put through an ion-exchange resin to remove the cations and release the carboxylic groups, then the titratable acids will be the same as the total acid present.

In the wine industry, titratable acidity is measured automatically by auto titration.

Balancing wine acidity

The taste and stability of a wine depends upon the acidity of the wine. Wine should have a pH of 3.1–3.5. This range is optimum for fermentation and ensures the desired balance of sugar and acid. Higher pH values (above pH 4.2) may allow bacteria to multiply.

The acidity of wine is due to the weak acids, particularly tartaric, malic and citric acids. Weak acids ionise only partially in water. It is not easy in wine to determine the percentage ionisation for these acids, particularly tartaric acid. The percentage ionisation depends upon the K_a and the pH as shown in Table 1.4. All three forms of these organic acids are found in wine.

Table 1.4 Ionisation percentage of the main acids found in wine at two pH values

pH	Species at equilibrium	Tartaric acid	Malic acid	Citric acid
3.0	H_2A	51.3	74.1	57.6
	HA^-	46.7	25.7	41.7
	A^{2-}	2	0.2	0.7
3.5	H_2A	23.4	47.1	29.3
	HA^-	67.5	51.7	67.1
	A^{2-}	9.1	1.2	3.6

Changing the acidity



To learn more about buffers, refer to Chemistry section 2.6, page 199.

If the pH of the wine is too high, then the total acidity of the wine can be increased by adding tartaric acid. Tartaric acid is the most common acid in wine, and is stable and less likely to be attacked by bacteria.

If the pH of the wine is too low, then the wine may be inoculated with of culture of lactic acid bacteria. This second fermentation (malolactic fermentation) converts the diprotic acid (malic acid) to the monoprotic acid (lactic acid). Alternatively, substances such as $KHCO_3$, $CaCO_3$ or K_2CO_3 can be added that cause potassium hydrogen tartrate or calcium tartrate to precipitate.

Working out how much tartaric acid or calcium carbonate to add to bring about the desired change in pH is difficult, as wine will resist some changes. This is due to the presence of buffers and is called the buffering capacity of the wine. Buffers will maintain the pH of the solution within one pH unit. The major acid that acts as a buffer is tartaric acid.

In practice, the winemaker adds a certain small amount of either the acid or the base and then measures the pH before making a second addition.

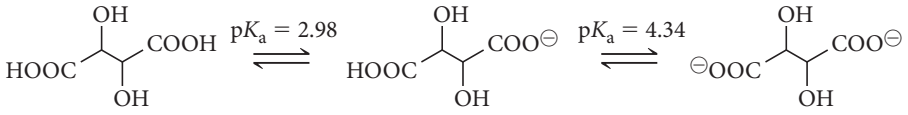
The strongest organic acid in wine is tartaric acid. Tartaric acid makes the greatest contribution to the pH of wine. It is partially ionised to two H^+ ions and the tartrate anion ($C_4H_4O_6^{2-}$) in two steps:

$$C_4H_6O_6 + H_2O \rightleftharpoons C_4H_5O_6^- + H_3O^+ \quad (1)$$

(H_2T) (HT^-)

$$C_4H_5O_6^- + H_2O \rightleftharpoons C_4H_4O_6^{2-} + H_3O^+ \quad (2)$$

(HT^-) (HT^{2-})



Tartaric acid (H_2T) Hydrogen tartrate (HT^-) Tartrate (T^{2-})

◀ **Figure 1.12**
Tartaric acid ionises in two steps to tartrate.

If the pH of the wine is too high, then more tartrate anion is produced, a reaction that produces more hydronium ions as well. If the pH is too low, then tartaric acid is produced, a reaction that consumes hydronium ions – when the concentration of hydronium ions is lower, so pH is higher. This helps maintain the pH of the wine. Buffers partially counteract the winemaker's attempts to change the pH.

Tartaric acid is also present in the form of its salts; the most important is potassium tartrate (KHT) (tartar, or cream of tartar in cooking). This dissociates in water to form hydronium ions, potassium and tartrate ion (HT^-):

$$KC_4H_5O_6 + H_2O \rightarrow C_4H_5O_6^- + H_3O^+ + K^+$$

(KHT) (HT^-)

The potassium tartrate salt (KHT) is soluble in grape juice but as ethanol is formed its solubility decreases. Wine becomes a supersaturated solution of this salt. This is called tartrate instability. At low temperatures, the salt may precipitate out of the wine. This is the harmless sediment that is observed at the bottom of a wine bottle. Winemakers 'superchill' the wine before bottling in a process called **cold stabilisation**. The KHT precipitates, reducing its concentration in the wine and reducing the probability of the sediments forming later in the bottles. Small crystals of potassium hydrogen tartrate are sometimes added to provide **nucleating points** for crystals to precipitate the KHT.

If the wine pH $\geq$ 3.9, then cold stabilisation causes an increase in pH. But if the wine pH $<$ 3.9, then cold stabilisation causes a decrease in pH. This can be explained by Le Chatelier's principle. At pH $<$ 3.9, the first reaction (1) dominates – cold stabilisation removes HT^- from solution, thus lowering its concentration. The system tries to partially oppose this change by shifting the equilibrium to the right, producing more HT^- and H_3O^+. The production of H_3O^+ therefore decreases the pH of the wine.

To learn more about dynamic equilibrium, refer to Chemistry section 1.3, page 146.

Revise how to control equilibrium in Chemistry section 1.4, page 162.

When wine pH ≥ 3.9, the equilibrium reaction between the tartaric anion (HT^{2-}) and the hydrogen tartrate form (HT^-) is the main reaction (2) (Table 1.5 and Figure 1.12 show that HT^- is the most common species present). When the concentration of HT^- is reduced, then the system tries to partially oppose the change by shifting the equilibrium to the left. This consumes the free H^+ ions and HT^{2-} and produces more HT^- and the pH of the wine increases.

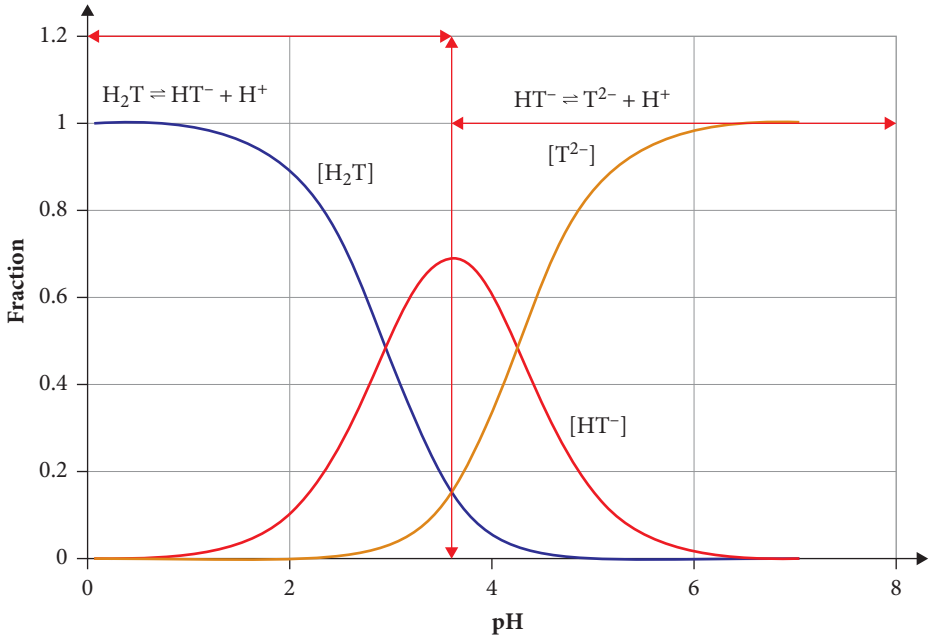


Figure 1.13 ▶ The main species of tartaric acid present in wine at various pH levels

ACTIVITY 1.3

BUFFER CAPACITY OF WINE

Aim

To explore the buffering capacity of three different wines and to comment on the buffering capacity of each

You will need

- Calculator
- Spreadsheet software such as Microsoft Excel or graph paper

What to do

The following table shows the reduction in pH when $2\,g\,L^{-1}$ of tartaric acid was added to three different wines. This was repeated three times, giving a final total of $8\,g\,L^{-1}$ of tartaric acid in each wine.

Wine	Starting pH	pH after tartaric acid addition			
		$2\,g\,L^{-1}$	$4\,g\,L^{-1}$	$6\,g\,L^{-1}$	$8\,g\,L^{-1}$
White	4.0	3.8	3.5	3.3	3.0
Rosé	4.0	3.9	3.7	3.5	3.3
Red	4.0	4.0	3.9	3.7	3.5

Plot the pH values for the three different wines.

What did you discover?

1 Comment on the buffering capacity of each wine.

2 What does this indicate about the composition of red, rose and white wines?

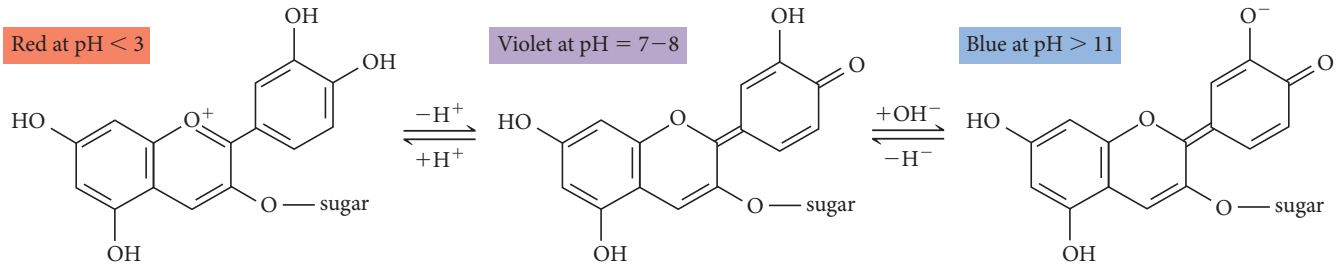
The wine matrix

Wine is not a just a solution of acid, alcohol and sugars. It has a matrix of many different compounds that give the wine flavour, aroma and colour. These compounds are esters, different alcohols, **anthocyanins** and tannins, which give the wine 'character'.

Tannins are a group of phenol compounds called **polyphenols**. These molecules affect the wine's colour, ageing and texture. They are responsible for the astringency (sharp taste that makes the mouth dry or 'pucker') in wine and play a crucial role in the way the wine ages. Tannins exist naturally in the skins, seeds and stems of grapes. Red wines are fermented with the grape skins and seeds, which explains why red wines have high tannin content. Normally, fermentation occurs in stainless steel tanks. But some chardonnay wines undergo fermentation in oak barrels and owe part of their taste to tannins transferred from the wooden barrels.

To learn more about esters and aromatic compounds, refer to Chemistry section 6.1, page 280.

▼ **Figure 1.14**
Cyanidin, a phenolic compound found in wine, has different forms (structures) and different colours at different pH values.

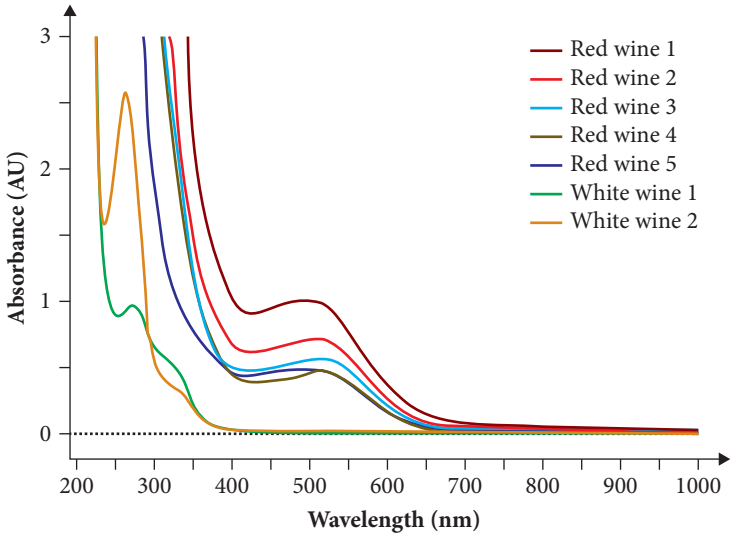


Colour

The phenolic compounds contribute to the colour and flavour of grapes. Phenolic compounds are aromatic compounds in a six-carbon aromatic benzene ring that have one or more hydroxyl groups (−OH) attached. Phenolic compounds can be different colours at different pH values, as shown for cyanidin in Figure 1.14. They can be grouped by colour, such as anthocyanin (which can be red, blue or purple), or molecular structure, such as the flavones (which have a particular backbone structure). Polyphenols are antioxidants that protect the plant from UV (ultraviolet) light damage.

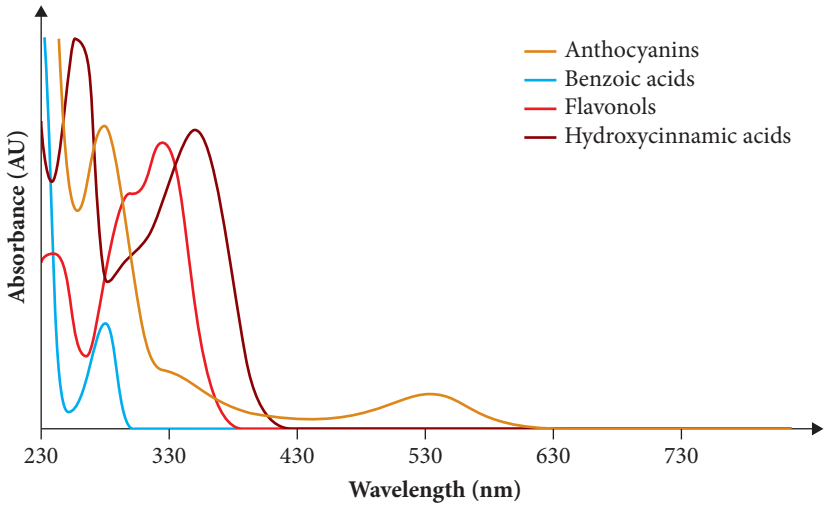
By maintaining the pH within the range 3–3.5, the winemaker can optimise the colour of the wine.

UV–visible spectroscopy measures the phenolic compounds present. Each variety of wine has a characteristic phenolic composition or 'phenol fingerprint'. UV–visible spectroscopy can be used to determine the total phenolic extract (280 nm), flavones (320 nm), phenolic acids (360 nm) and total anthocyanins (520 nm). This analysis is cheap and fast, with measurements being made in minutes.



◀ **Figure 1.15**
Absorbance spectra of wine samples

Figure 1.16 ▶
Absorbance spectra of various phenolic compounds found in wine



WOW

Good or bad?

There have always been claims about the health benefits of wine. Egyptians used wine as medicine. The Ancient Greek physician Hippocrates, the 'father of western medicine', promoted wine as part of a healthy diet. At the time, drinking water was not safe. Diseases such as cholera were transmitted by drinking water until sanitation systems were developed.

In most countries, a diet high in saturated fats is associated with fatal coronary disease. Not so for the French. The French drink moderate amounts of red wine. Red wine has high levels of antioxidants such as anthocyanin and **resveratrol**. These compounds are being studied to see if they are responsible for the benefits of a moderate consumption of red wine. Red wine is thought to have benefits for the heart, mental health, provide protection against certain cancers and promote a longer life.



To understand more about the instrumental technique of UV–visible spectroscopy, refer to Chemistry section 8.6, page 397.

The type and amount of tannins in wine can be detected by a range of instruments. Chromatography techniques can separate the components. These methods are quick as they require little or no sample preparation unlike the earlier traditional methods. Infrared spectroscopy is also commonly used to analyse grape and wine colour components. This technique requires little preparation. The 'fingerprint region' in the spectrum at 900−1600 cm^{-1} is used by the winemaker to monitor the winemaking process.

Scientists at the Australian Synchrotron have studied the degree to which tannins are soluble and how they interact with the 'wine matrix', shaping the wine character. The synchrotron is essentially taking X-rays of the structure of tannins in solution, which will help the winemaker's understanding of how to manage tannin in both the vineyard and the winery.

Taste

The flavour of the wine is influenced by residual sugars, amount of alcohol, acidic compounds and tannins and whether the wine is sparkling or not.

Wine-tasters check for the astringent sensation on the tongue, gums and cheeks. This is a check for the tannins that react with saliva, causing the drying ('puckery') sensation. The complexity of the flavours results in descriptions of the wine such as 'packed with enticing fruit aromas of peach, melon and grapefruit, seamlessly followed by a palate with a soft creamy texture, subtle oak and a lingering finish'.

WOW

Not from there!

Judging the aroma, flavour and taste of wine is difficult and subjective. Early Australian winemakers faced many difficulties, including prejudice. At the 1873 Vienna Exhibition, the French judges, tasting blind, praised some wines from Victoria. But when it was revealed that the wine came from Australia, they withdrew in protest on the grounds that wines of that quality clearly must be French.

Aroma

The aroma of the wine is the odour that originates from the grape. The aroma is affected by the grape variety and growing season. The **bouquet** of the wine consists of the odours that are due to the fermentation process and ageing, particularly those that develop after bottling.

There are many chemicals that are responsible for the odours, including esters, alcohols, aldehydes and ketones, nitrogen-containing compounds and sulfur-containing compounds. During fermentation, esterification reactions between alcohols and carboxylic acids may occur. The fruity sweet-smelling compounds produced are called esters.



To learn more about esters, refer to Chemistry section 6.9, page 310.

ACTIVITY 1.4

ESTERS IN WINE

Aim

To determine the carboxylic acids and alcohols that produce the typical esters found in wine

Table 1.5

Ester	Associated aroma
Methyl butanoate	Apple
Ethyl butanoate	Pineapple
Propyl ethanoate	Pear
Pentyl ethanoate	Banana

What to do

1 Examine the esters in Table 1.5.

2 Extend the table by adding a third column and show the chemical structure for each ester.

What did you discover?

1 Determine the carboxylic acid and alcohol required for its formation.

2 Explain which ester you would expect to be the most common in wine.

3 How you would confirm which ester was the most common?

Maintaining the balance

Sulfur dioxide is used to kill or inhibit unwanted yeasts and bacteria in wine, and to protect the wine from oxidation. The winemaker can achieve the perfect chemical balance of sugar, alcohol, acidity and colour. But if the wrong micro-organisms or oxygen are added, the wine may be ruined. Sulfur dioxide was first used in winemaking by the Romans. They discovered that if candles made of sulfur were burnt in empty wine vessels, the vessels would keep fresh and not gain a vinegar smell. Sulfur dioxide is the most important additive used in winemaking.

Wine can be made without adding sulfur dioxide. Every wine contains sulfur dioxide as yeast produces a small amount of about 10 ppm during fermentation.

Sulfur dioxide is a gas that is highly soluble in water. This is an exothermic process. When SO_2 is added to wine, it reacts with water to form hydrogen sulfite:

$$SO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)$$

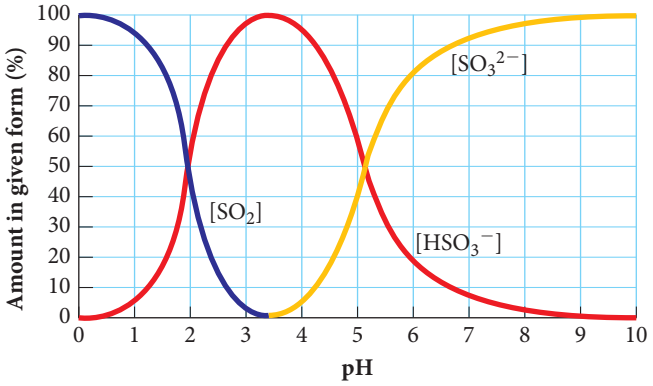
The hydrogen sulfite will further react with water, forming H_3O^+ and sulfite (SO_3^{2-}) ions:

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_3^{2-}(aq)$$

When sulfur dioxide is added to wine, there are three forms present: molecular SO_2, SO_3^{2-} and HSO_3^-. The quantity of these fractions depends on the pH of the solution. At normal wine pH (3–4), hydrogen sulfite (HSO_3^-) is the most common. At high pH, the equilibrium is pushed so far to the right that the predominant form is SO_3^{2-}.

At low pH, the equilibrium favours the SO_2 form.

Figure 1.17 ▶ The various species or forms of SO_2 present in wine at different pH values

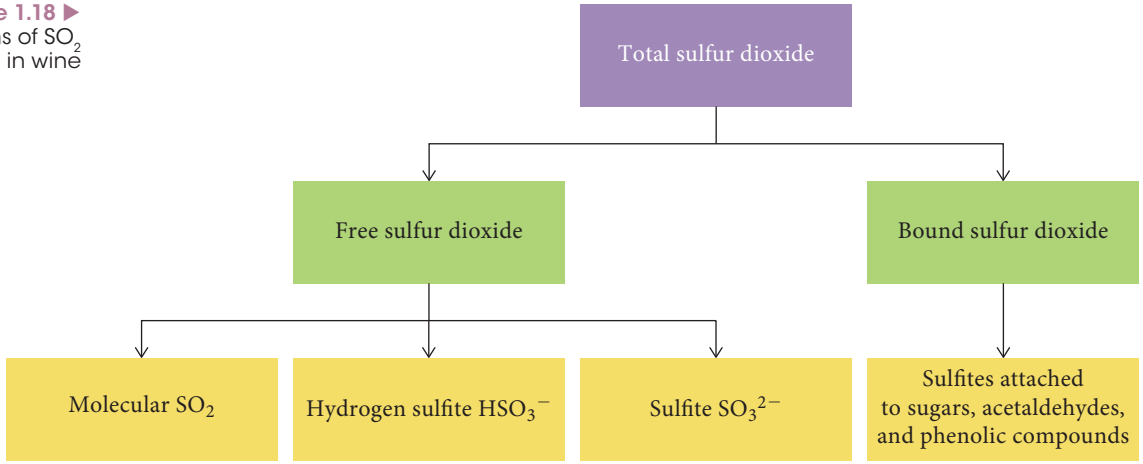




To learn more about the competing equilibrium reactions involving weak acids, refer to Chemistry section 2.5, page 194.

When the SO_2 is added to wine, a portion binds with other compounds in the wine. This portion is called 'fixed' or **bound SO_2**. The remainder is called **free SO_2**. The total SO_2 is the sum of the free and the bound SO_2. Molecular SO_2 is far more efficient than HSO_3^- in inhibiting bacteria and yeast growth.

Figure 1.18 ▶ The different forms of SO_2 found in wine



Winemakers can add sulfur dioxide in three different ways:

1 The sulfur dioxide gas may be liquefied and added to the crushed grapes.
2 The sulfur dioxide may be dissolved in water and added to the crushed grapes as a mixture of sulfurous acid and dissolved sulfur dioxide.
3 Salts of sulfur dioxide such as metabisulfite ($K_2S_2O_5$) may be added. The sodium form of this salt can be added as well but the potassium salt is preferred because the potassium ion helps tartaric acid to precipitate and does not leave a salty taste.

When potassium metabisulfate dissociates in water, ionised hydrogen sulfite is formed:

$$K_2S_2O_5 + H_2O \rightarrow 2K^+ + 2HSO_3^-$$

Potassium metabisulfate + water → potassium ions + ionised hydrogen sulfite

The wine bottle is a closed system, so equilibrium will be established between SO_2, HSO_3^- and SO_3^{2-}. When equilibrium is established at a particular temperature, there is the same ratio of free SO_2 despite the initial form added.



EQUILIBRIUM

Visit this website to learn about equilibrium and the wine industry. View the interactives to determine bound and free SO_2.

Determining sulfur dioxide levels

Knowing both the amount of free and total sulfites is important because only the free forms of sulfites play a preservative role in wine. This is often expressed as 'ppm free SO_2/ppm total SO_2' to denote which number is free and which is total. A redox titration of the wine using iodine with starch as the indicator can be used to measure the free SO_2.

The total SO_2 can also be determined by titration. This requires the additional step of adding sodium hydroxide to break down the complexes binding the SO_2. Table 1.6 lists the sulfur dioxide levels in white wine at different pH values. The values for red wine must also take into account whether the malolactic fermentation is to occur and the reaction of sulfur dioxide with the anthocyanins present.

SULFITE CALCULATOR

Use the online sulfite calculator that can help winemakers determine how much sulfur dioxide or potassium sulfite to add to wine.

Table 1.6 Free SO_2 required in mg/L for 0.8 mg/L molecular SO_2

pH	Free SO_2 ($mg\,L^{-1}$)
3.00–3.20	10–20
3.21–3.40	20–30
3.41–3.50	30–50
Above 3.5	50–150

Note: A molecular SO_2 level of 0.8 mg/L is suggested as an effective level for inhibition of wine spoilage. The three different fractions or forms of free SO_2 depend on pH.

To learn more about oxidation and reduction reactions, refer to Chemistry section 3.2, page 207.

The maximum legal limit for total sulfur in Australia for a dry wine is $250\,mg\,L^{-1}$ and for a sweet wine it is $300\,mg\,L^{-1}$. Sulfur dioxide is an allergen and should be avoided by people with asthma.

Antimicrobial role of sulfur dioxide

Spoilage bacteria and yeast that can adversely affect a wine's flavour are sensitive to some degree to sulfur dioxide. At low concentrations, SO_2 will inhibit the growth of the bacteria, wild yeast or moulds. At high concentrations, SO_2 will kill these organisms. Commercial yeasts are more tolerant than wild yeasts of SO_2.

Antioxidant role of sulfur dioxide

Sulfur dioxide acts as an antioxidant. Oxygen (O_2) is highly electronegative and will scavenge electrons from other molecules, becoming reduced to O^{2-}. This reaction oxidises the other molecules. It sets in a motion a series of unwanted reactions. Sulfur dioxide can react with the precursors of these oxidative reactions, which prevents them from reacting with oxygen. Sulfur dioxide may also bind with compounds already oxidised, stopping any further reactions. Sulfur dioxide also reduces the activity of the oxidative enzymes such as polyphenol oxidase.

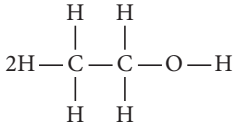
To learn more about these reactions of oxidation and redox reactions, refer to Chemistry section 6.6, page 302.

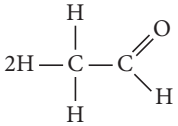
Stopping further reactions

Ethanol can be oxidised to ethanoic acid if oxygen is present. This occurs in two steps:

Step 1

$2C_2H_5OH + 2O_2 \rightarrow 2CH_3CHO + 2H_2O$

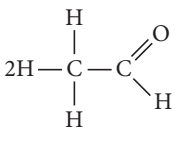


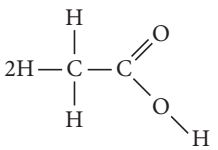


Ethanol + oxygen → ethanal (acetaldehyde) + water

Step 2

$2CH_3CHO + 2O_2 \rightarrow 2CH_3COOH$





Ethanal + oxygen → ethanoic acid (vinegar)

Sulfur dioxide binds to the ethanal (acetaldehyde), which prevents the second step occurring. This is an example of sulfur dioxide reacting with a compound that has been oxidised and stopping any further reactions.

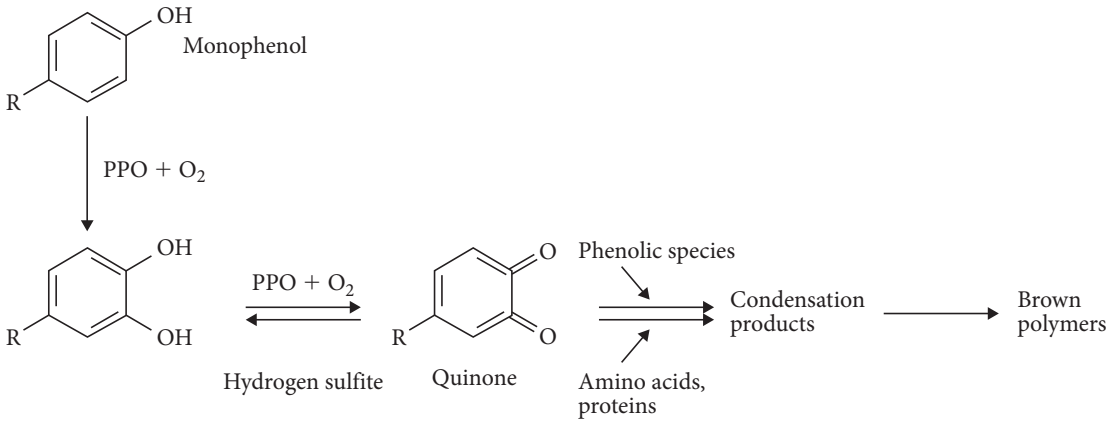
The phenols in wine can be oxidised to form **quinones**. Hydrogen peroxide (H_2O_2) is produced as a by-product. Hydrogen peroxide is a stronger oxidant and will react more readily with ethanol to produce ethanoic (acetic) acid. However, the sulfite reacts with the peroxide preventing further oxidation of ethanol:

$$SO_3^{2-}(aq) + H_2O_2(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(l)$$

Sulfur dioxide: reacting with the enzymes

Enzymes such as polyphenol oxidase (PPO) are present in all fruit. These enzymes are responsible for the browning of freshly cut fruit and will readily catalyse the oxidation of phenolic compounds in wine. This is a multistep process. Hydrogen sulfite can reduce the formation of brown compounds as it inhibits the action of the enzyme PPO and by favouring the conversion of the quinone back to a phenolic compound as shown in Figure 1.19.

Figure 1.19 ▶ The enzyme PPO allows the formation of chemicals that make fruit go brown.



ACTIVITY 1.5

REDOX PHENOMENA IN WINE

Aim

To construct an electrochemical series of the redox reactions in wine

You will need

- Calculator
- Computer with internet access
- This textbook

The standard reduction potential for biochemicals can be difficult to find, so if needed use these:

$CH_3CHO + 2H^+ + 2e^- \rightarrow CH_3CH_2OH$ $\quad E^\circ = -0.2$ V

$CH_3COOH + 2H^+ + 2e^- \rightarrow CH_3CHO + H_2O$ $\quad E^\circ = -0.185$ V

$2CO_2 + 12H^+ + 12e^- \rightarrow CH_3CH_2OH + 3H_2O$ $\quad E^\circ = -0.085$ V

What to do

1. Starting with sulfur dioxide's reaction with water, classify each reaction as an acid–base reaction and/or a redox reaction.
2. Construct the pathway for the production of alcohol from sugars to the undesirable ethanoic acid, using the information in the previous section. Classify these reactions as acid–base or redox.
3. For each redox reaction, identify the conjugate pairs (exclude the reactions with the enzymes).
   - a For each redox reaction, calculate the oxidation number for any sulfur or carbon atoms.
   - b Write the half equations for the reactions.
   - c Search for the standard reduction potential for each reaction.
   - d Combine the reduction equations to form an electrochemical series.

What did you discover?

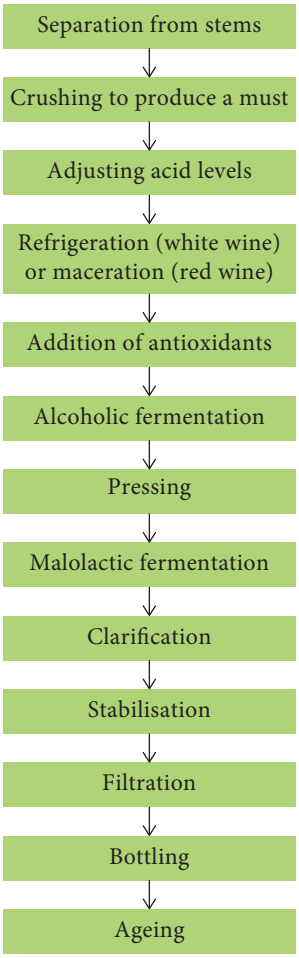
1 What is the electrochemical series for wine?
2 Which is the strongest oxidant?
3 Which is the strongest reductant?
4 Does sulfur dioxide's role as an antioxidant involve any direct redox reactions? Explain.

Making wine – white versus red

Winemaking starts with the grapes. Once grapes are ripe and ready to harvest, they will be subjected to different processes depending on the variety of grape and the desired type of wine.

The following steps are involved in commercial winemaking.

1 Grapes are separated from the stems and the other parts of the vine. The stems have very high tannin content.
2 The grapes are crushed to extract the juice. This mixture of solids and liquid is called the **must**. The must for a red wine stays in contact with the grape skins for longer than the must for a white.
3 The must is analysed for acids and sugars. If required it is adjusted for acids.
4 If required other substances such as tannin, enzymes and yeast nutrients are added.
5 White wine must is separated from the grape skins and refrigerated (to cause the remaining sediment to drop to the bottom). Red wine undergoes **maceration**, a process in which it stays in contact with the grape skins to leach out colours and flavours.
6 The must is treated with sulfites or alternative antioxidants or microbial chemicals.
7 The must is inoculated with yeast and fermentation occurs. Once the alcohol level reaches 8–9 per cent, it is considered wine. The temperature, sugar and alcohol levels are all controlled because they affect the activity of the yeast.
8 The skins are removed from the red wine during **pressing**.
9 If the acid level of red wine is too high, malolactic fermentation may be completed.
10 The wine is clarified (removing suspended particles) by processes such as cold stabilisation.
11 The wine is stabilised with sulfite and tartaric acid.
12 The wine is filtered and bottled.
13 Some wines are aged further.



▲ **Figure 1.20**
A flowchart for the winemaking process

Alcohol in the blood

When an alcoholic beverage is consumed, alcohol is absorbed by the blood and transported through the body. Ethanol is a small molecule that is soluble in both fats and water. So 10–20 per cent of the alcohol consumed is directly absorbed through the stomach.

The effect of the alcohol depends on its concentration – the BAC (blood alcohol concentration). The BAC depends on the amount of alcohol drunk and the volume of blood in the person. Ethanol is a toxin – it supresses the activity of nerve cells, making the person sluggish or slow to react. This is why there are legal limits on blood alcohol concentration for drivers of cars, trucks and boats. At 0.03 per cent, the person has trouble with fine movements and has decreased inhibitions; at 0.10 per cent, speech starts to be slurred; at 0.20 per cent, the memory may be blacked out; and at 0.40 per cent, death is likely. In large amounts, ethanol may induce a coma and respiratory failure. The body tries to remove the ethanol by vomiting. Most alcohol deaths are a result of suffocation from one's own vomit.

Standard drink

In Australia, one **standard drink** is the volume of beverage that contains 10 grams of ethanol at 20°C. A standard drink takes into account that different alcoholic beverages have different alcohol levels. To reduce health risks, particularly to the liver, healthy adults should limit their alcohol intake to two standard drinks a day.

Two different people may consume the same number of standard drinks but have different BAC when tested. This is because each person is a different weight and metabolises the ethanol differently. In drinking one bottle of red wine, approximately 80 grams of ethanol is digested. How long it takes to drink the whole bottle will have a dramatic effect on the BAC.

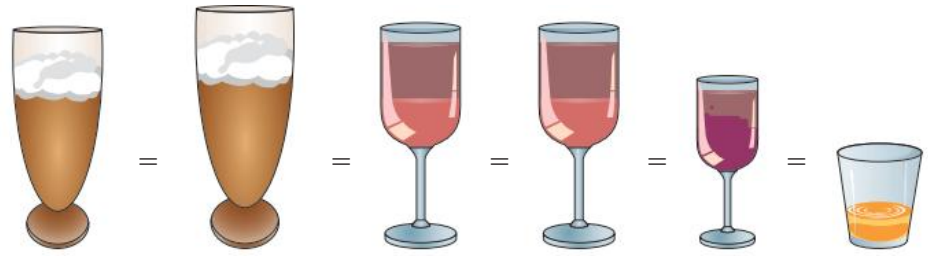


Figure 1.21 ▶
Each of these standard drinks has the same amount of ethanol (10 grams).

STANDARD DRINKS

Visit this website to learn more about standard drinks and take a quiz.

Sobering up

A healthy adult can remove about one standard drink per hour by breaking down the alcohol in the liver. Ethanol (CH_3CH_2OH) is oxidised to form acetaldehyde (CH_3CHO, ethanal), which is further oxidised to ethanoic acid (CH_3COOH). Ethanoic acid can be used to make fatty acids or ultimately broken down to carbon dioxide and water. A small percentage of alcohol is excreted via the kidneys in the urine or exhaled via the lungs when breathing.

Other compounds present in wines and alcoholic beverages will also be removed by the liver. It is thought that these compounds, in particular ethanal, cause hangover symptoms. Ethanal is more toxic than ethanol.

WOW

Elephants and red wine

The Europeans of 1255 did not know what to make of the elephant. This exotic animal was given by Louis IX of France to Henry III of England for his menagerie in the Tower of London. Unsure how to treat the elephant, its carers gave it a gallon of red wine a day to warm its blood in winter. It died in 1257 from drinking too much wine. The next elephant was not treated much better. It was owned by Charles I in 1623 and was also given a gallon of wine a day.



Figure 1.22 ▲
Tower of London elephant presented to Henry III in 1255

Breathalysers

Blood alcohol concentration can be estimated by breath tests. The amount of alcohol in exhaled air (in the breath) is proportional to the amount in the blood. The ratio is 1:2100. The earliest blood alcohol meters used a chemical reaction that produced a colour change. Ethanol reduced the orange dichromate ion $Cr_2O_7^{2-}$ to the green chromium(III) ion Cr^{3+}. The degree of colour change is proportional to the amount of ethanol present.

Current breathalysers still involve the oxidation of the ethanol to ethanoic acid. These breathalysers are mini fuel cells and the electrical current produced is proportional to the alcohol level present.

Breathalysers may also use infrared spectroscopy to detect the –OH part of the alcohol as the molecules vibrate.

When a driver is found to have a high BAC by breathalyser, a blood test may be performed. The blood test uses gas chromatography. It has been argued in court that other components interfere with the fuel cell breathalyser result. As each component has a specific R_t, gas chromatography eliminates this defence. Additionally, the blood test discounts the argument that the breath test is just testing the alcohol in the mouth.

To learn about oxidation states, refer to Chemistry section 3.5, page 218.

BREATHALYSERS

Visit this website to learn more about how breathalysers work.

Greening the wine industry

The wine industry is aiming to reduce chemical use in winemaking and viticulture. A particular environmental concern for the wine industry was contamination of waste water. Actions being taken to reduce this include:

- minimising the caustic chemicals used for cleaning
- using less hazardous chemicals as pesticides in the vineyard.

Reducing energy use and waste will also make wineries more sustainable.

The use of less hazardous chemicals as pesticides appears to be very effective in controlling the vine mealybug, which sits under the bark of the vine. Traditionally, large amounts of organophosphates have been applied to ensure direct contact with the pest. Some companies have now developed a safer alternative in the form of the female mealybug's pheromone. Pheromones are molecules that insects use to attract other insects of their species. Male mealybugs were attracted to traps containing a lethal pesticide. The pheromone had a couple of additional benefits – it also attracted the natural predators to the mealybugs and the natural predator populations were preserved, thus reducing the need for an additional pesticide spray later in the season.

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126) AC

Cork alternatives

Traditionally, winemakers used cork to seal the bottle. Cork is a natural product derived from the bark of the cork oak tree. Cork occasionally tainted the wine, which resulted in spoilage of the wine. Additionally, the supply of quality cork in 1980 was very limited and cork taint rates increased. In 2000, winemakers from the Claire Valley released their riesling wines under screw cap. Now the majority of Australian and New Zealand wines use screw caps. Cork manufacturers claim that cork is more sustainable.



Marekusz/Dreamstime.com

▲ **Figure 1.23**
Corks are no longer the preferred method of sealing bottles.

Bottle alternatives

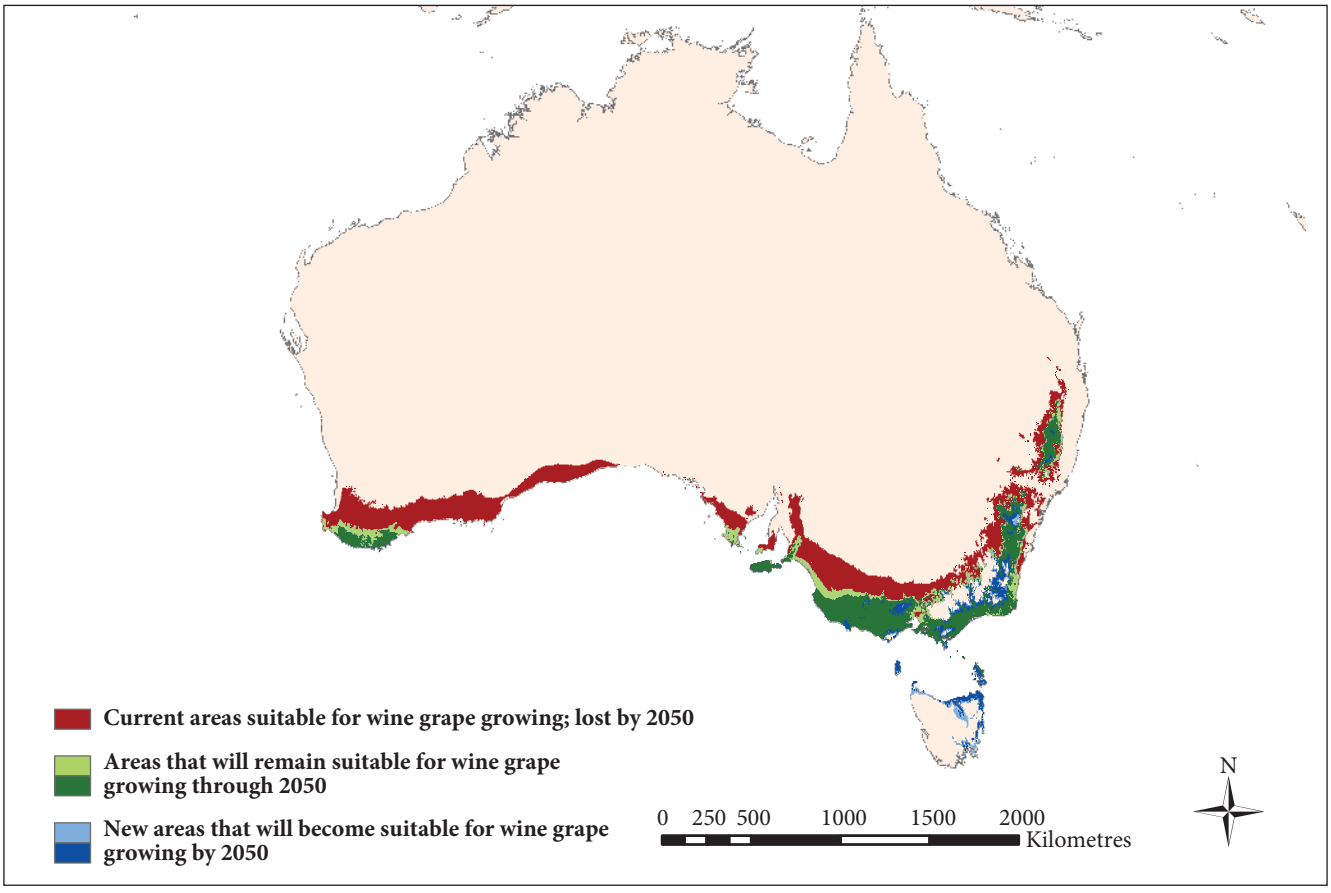
Glass is the traditional material used for wine containers. Glass can be recycled, but it is heavy. This means the energy and carbon footprint used in transporting the bottles is high. Lighter weight materials such as the plastic PET (polyethylene teraphthalate) could be used for bottles. These have to be treated with an oxygen barrier to enhance shelf life. The bottles weigh about 50 grams, which is about 10 per cent of the weight of a glass bottle. Another alternative is the wine cask. This holds 80 per cent more wine and is less than two-thirds the weight of the equivalent volume of a glass bottled wine. The wine cask released by the Yalumba winery in 2013 has a carbon footprint that is 13 per cent of that of a glass bottle.

Global warming – facing the challenges

To learn more about green chemistry, refer to Chemistry section 9.7, page 424.

Wine production relies on the quality of the grapes, which depends upon the climate they are grown in. Generally, cooler climates are preferred for wine production; those that are warm enough to stop frosts but cool enough to keep sugar production sufficiently low. Excess sugars make the wine too sweet and result in alcohol levels that are too high. Grapes produced in cooler climates ripen earlier, producing a fresher more acidic harvest. Each variety has its specific requirements, but generally vines need 1300–1500 hours of sunshine during the growing season and around 690 mm of rain. If the climate is too warm, raisins rather than wine grapes will be made.

It is not surprising that there are concerns when the climate changes. Researchers have predicted a two-thirds fall in production in the world's premier wine regions. Australia is facing a dramatic change (Figure 1.24). Some wineries are shifting to cooler areas like Tasmania. Western Australian vineyards are already reporting the introduction of water saving techniques. Other producers are using alternative energy sources, reducing their greenhouse emissions and planting extra trees and shrubs to act as carbon sinks. Other producers are switching to hotter climate grape varieties or shading the grapes.



Courtesy of Lee Hannah and Patrick Roehrdanz

Figure 1.24 ▲ The effect of climate change on wine production

Organic wine

Chemists would define all wine as organic because wine is based upon carbon compounds; in chemistry, organic materials are those containing carbon (except carbonates, carbon dioxide and carbon monoxide). However, this is not the definition used by the general public: the word 'organic' is often associated with foods that have been grown or produced without pesticides or additives.

Organic wine is produced from grapes that are grown using only products derived from natural sources. The term 'organic wine' means the use of any chemicals in the winemaking process is minimised and each chemical must be certified organic and from a natural source. This means organic wineries also avoid chemical cleaners. Equipment hygiene is maintained through the use of certified organic products or hot water and steam.

Sulfites must be kept to low levels in organic wine. Organic wines are less stable so have a shorter shelf life. This is more of a concern with red wines as they are normally cellared for a longer time. People who are allergic to sulfites may not be affected by drinking organic wine.

ACTIVITY 1.6

SUSTAINABILITY IN THE WINE INDUSTRY

Aim

To evaluate the environmental, social or economic impact of a sustainable practice for the wine industry such as organic wine, green chemistry practices, use of plastic bottles, wine casks or corks

You will need

- Computer with internet access

What to do

1. Read the article located in the weblink Sustainable wines.
2. Select another winery and search its website for the sustainable practices that they are using.
3. Select a topic to research. Check with your teacher that your topic is suitable.

What did you discover?

1. Explain what the wineries are doing to increase their sustainability.
2. What are some of the issues the wineries are facing in this task?
3. Are all the wineries solving the problem in the same way?
4. Where are the wineries getting their information from to inform their decisions?
5. Are the consumers responding positively to the changes?
6. Is the practice helping the sustainability, environmental or social impact of the wine industry?

SUSTAINABLE WINES

Read the article about growing grapes sustainably.

TAYLORS WINES

Read about one winery's approach to environmental management.

CHAPTER SUMMARY

- Wine is produced by the fermentation of grapes. It is a sophisticated solution of alcohol, sugar, acids and various components that influence the colour, taste and aroma of the wine.
- Techniques such as titration, gas chromatography, NMR spectroscopy, mass spectrometry and infrared and UV-visible spectroscopy are used to analyse the chemical composition of wine. Scientists use the data to identify how the various chemicals are related to each other and how they affect the quality of the wine.
- Winemakers balance the acidity, alcohol concentration, sugar levels and colour of the wine. This balance is influenced by two key reversible reactions.
- The main acid in wine is tartaric acid. This acid and its salts contribute to the 'tartrate instability' of wine and are the main chemicals responsible for the 'buffering capacity' of the wine.
- Sulfur dioxide maintains the chemical balance in wine by acting as an antioxidant by binding with ethanal. The amount of 'free' SO_2 is determined by the pH of the wine.
- The wine industry is facing market and climate forces. It is responding to this by applying the chemical knowledge of green chemistry for sustainability and in the development of 'organic' wine.

CHAPTER GLOSSARY

aged refers to wine that has been stored to develop flavour and complexity. Wine can be aged in barrels or bottles. Red wines are aged for longer. White wines are drunk 'younger'.

anthocyanins molecules that give the colour to wine

astringency the sharp taste that makes the mouth dry or 'pucker'

aroma the odour that originates from the grape; it is affected by the grape variety and growing season. Can also refer to the bouquet

bound SO_2 sulfur dioxide that is combined with other substances such as sugars and anthocyanins; is not available to work as a preservative

bouquet the odours of the wine that arise due to the processing of wine, including fermentation and ageing

cold stabilisation a process that helps prevent sediments forming in bottled wine as it causes the precipitation of potassium hydrogen tartrate from the wine before bottling

fermentation an exothermic process that typically involves breaking down of carbohydrates in fruits and grains to form alcohols or acids in the absence of oxygen; in wine, yeasts convert sugars to ethanol and carbon dioxide

free SO_2 sulfur dioxide that can work as a preservative

glucophilic enzymes that react preferentially with glucose rather than fructose

inverted sugar a sugar produced from the hydrolysis of the disaccharide sucrose to form the monosaccharides fructose and glucose

maceration a process in which grape juice is in contact with seeds and grapes for a period of time; this allows colours and flavours to leach out

malolactic fermentation a second fermentation usually in red wine that reduces the acid content; bacteria in the sediments convert the diprotic acid malic acid into lactic acid

must the combination of solids and liquids formed by crushing the wine grapes

nucleating point a substance that will cause the formation of crystals in supersaturated solutions

oenologist a winemaker

oenology the science of wine making

phenolics aromatic compounds in which one or more hydroxyl groups (–OH) are attached to a six-carbon aromatic benzene ring

polyphenols a group of aromatic compounds that comprise many phenol molecules covalently bonded

pressing the process of extracting juices from grapes and must; removes the skin and seeds from the wine

quinones organic compounds that have a six-membered ring with two C═O groups in the ring; they are derived from aromatic compounds such as benzene

residual sugar the sugars remaining in wine after fermentation. Some sugars cannot undergo fermentation. If fermentation is stopped early, then the unreacted sugars will also be included in the residual sugar

resveratrol a phenolic compound found in grape skins and seeds and is believed to have health benefits

standard drink the volume of a drink that contains 10 grams of ethanol when measured at 20°C

tannin a group of compounds that comprises many phenol molecules; they can bind with other molecules and are responsible for the astringency of wine. This group is important for the ageing of wine

titratable acidity the total amount of acid present in wine as determined by titration

viniculture a specific branch of horticulture that involves the science, production and study of grapes for wine production

CONTEXT 2
CHEMICAL INDUSTRY



Shutterstock.com/Repina Valeriya

By the end of this chapter you will have covered the following material.

Science as a Human Endeavour

- People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk (ACSCH085 and ACSCH123)
- Science can be limited in its ability to provide definitive answers to public debate; there may be insufficient reliable data available, or interpretation of the data may be open to question (ACSCH086 and ACSCH124)
- International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region (ACSCH087 and ACSCH125)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCH088 and ACSCH126)

Contextual story – Chemical industry

- Metal production, purity testing and environmental issues
- Fertiliser production, purity testing and environmental issues
- Making useful chemicals

Chemical Understanding

- Energy from fuels
- Oxidation and reduction
- Electrolysis
- Molecule polarity
- Atomic absorption spectroscopy
- Volumetric analysis (titrations)
- Enhanced greenhouse effect
- Acids and bases (acid rain)
- Equilibrium
- Catalysts
- Reaction rates

Investigations

Context 2

- Activity 2.1 Interpreting a flowchart
- Activity 2.2 Production of other metals
- Activity 2.3 Production of other chemicals
- Activity 2.4 Investigating a major chemical spill

Chapter 1

- Experiment 1.1 Effect of changes to concentration on equilibrium
- Experiment 1.3 Effect of temperature on a system at equilibrium

Chapter 3

- Experiment 3.1 Metal displacement reactions

Chapter 5

- Experiment 5.2 Extraction of copper by electrolysis
- Investigation 5.1 Factors that affect electrolysis
- Investigation 5.2 Factors that affect the rate of an electrolysis reaction

Science as a Human Endeavour (SHE)

- People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk (ACSCH085 and ACSCH123)
- Science can be limited in its ability to provide definitive answers to public debate; there may be insufficient reliable data available, or interpretation of the data may be open to question (ACSCH086 and ACSCH124)
- International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia-Pacific region (ACSCH087 and ACSCH125)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCH088 and ASCSH126)

Science Understanding (SU)

- Over time, physical changes and reversible chemical reactions reach a state of dynamic equilibrium in a closed system, with the relative concentrations of products and reactants defining the position of equilibrium (ACSCH091)
- The effect of changes of temperature on chemical systems at equilibrium can be explained by considering the enthalpy changes for the forward and reverse reactions (ACSCH093)
- The effect of changes of concentration and pressure on chemical systems at equilibrium can be explained and predicted by applying collision theory to the forward and reverse reactions (ACSCH094)
- The effect of changes of temperature, concentration of chemicals and pressure on equilibrium systems can be predicted using Le Chatelier's principle (ACSCH095)
- Equilibrium position can be predicted qualitatively using equilibrium constants (ACSCH096)
- Acids are substances that can act as proton (hydrogen ion) donors and can be classified as monoprotic or polyprotic depending on the number of protons donated by each molecule of the acid (ACSCH097)
- The strength of acids is explained by the degree of ionisation at equilibrium in aqueous solution, which can be represented with chemical equations and equilibrium constants (K_a) (ACSCH098)
- Volumetric analysis methods involving acid–base reactions rely on the identification of an equivalence point by measuring the associated change in pH, using chemical indicators or pH meters, to reveal an observable end point (ACSCH102)
- A range of reactions, including displacement reactions of metals, combustion, corrosion and electrochemical processes, can be modelled as redox reactions involving oxidation of one substance and reduction of another substance (ACSCH103)
- Oxidation can be modelled as the loss of electrons from a chemical species, and reduction can be modelled as the gain of electrons by a chemical species; these processes can be represented using half-equations (ACSCH104)
- Electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction half-reactions connected via an external circuit that allows electrons to move from the anode (oxidation reaction) to the cathode (reduction reaction) (ACSCH107)
- Electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur, and can be used in small-scale and industrial situations (ACSCH111)

Science Inquiry Skills (SIS)

- Design investigations, including the procedure/s to be followed, the materials required, and the type and amount of primary and/or secondary data to be collected; conduct risk assessments; and consider research ethics (ACSCH075 and ACSCH113)
- Conduct investigations, including using volumetric analysis techniques and constructing electrochemical cells, safely, competently and methodically for the collection of valid and reliable data (ACSCH076)
- Select, construct and use appropriate representations, including half-equations, balanced chemical equations, equilibrium constants and expressions, pH, oxidation numbers, standard electrode potentials and cell diagrams, to communicate conceptual understanding, solve problems and make predictions (ACSCH079)
- Select and use appropriate mathematical representations to solve problems and make predictions, including calculating using the mole concept to calculate moles, mass, volume and concentrations from volumetric analysis data and calculating the pH of solutions of strong acids and bases (ACSCH080)
- Communicate to specific audiences and for specific purposes using appropriate language, nomenclature, genres and modes, including scientific reports (ACSCH081 and ACSCH119)

Chemical industry

When most people hear the word 'chemical', they tend to think of harsh, dangerous chemicals such as acids and bases. In reality, everything you come into contact with is a chemical. Every day you use a wide variety of substances produced by the chemical industry.

Chemicals range from pure metals such as copper to alloys such as steel and chemicals such as sulfuric acid, sodium carbonate, fertilisers and a range of acids and bases. Chemical reactions such as roasting, combustion and electrolysis are combined with physical processes such as distillation and crushing to convert a raw material into the required chemical.

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126) AC

Importance of the chemical industry

The chemical industry has significant economic, social and environmental impacts on Australia. The mining industry in Australia alone employs more than 2 per cent of the Australian population in a wide range of jobs including engineers, chemists, truck drivers and accountants. Add to this the chemical industry that produces both household and industrial chemicals for use here and for export and the number of jobs grows.



laboratory/Alamy



David Burton/Science Photo Library



Ashley Cooper pics/Alamy



Robert Kneschke/Shutterstock.com

▲**Figure 2.1**
A variety of jobs are available in the chemical industry:
a) chemist
b) engineer
c) truck driver
d) accountant.

Chemical industries contribute significantly to Australia's economy. Australia's chemical manufacturing industry alone contributes $11 billion to the Australian economy and makes up 11.5 per cent of the manufacturing industry.

There are also significant environmental impacts; for example, the emission of carbon dioxide from the burning of fossil fuels contributes to the enhanced greenhouse effect. Waste products such as sulfur dioxide and fertiliser run-off lead to environmental problems such as

acid rain and eutrophication of waterways, causing algal blooms. Companies in the chemical industry must combat environmental issues and have measures in place to prevent chemical spills and accidents.

Definitions

In order to understand more about the chemical industry, it is important to be familiar with some of the terms that are commonly used.

- A **raw material** is a material that is readily available but not highly processed. It is converted into the final product by chemical and physical processes. Raw materials include air, sand, coal, seawater, metal ores, salt, natural gas, limestone and other silicate materials. Raw materials are usually cheap and easy to obtain. Chemical plants are often situated near the site of raw materials to save on transport costs.

Figure 2.2 ▼
a) Coal and b) salt (sodium chloride) are some raw materials used in chemical production.



Michael Melford/The Image Bank/Getty Images



FLPA/Alamy

- An **ore** is a mixture of chemicals in which one of the chemicals is present in sufficient amounts to have a commercial value. Ores are usually mined and often contain metal oxides or metal sulfides. From these, a metal will be extracted and refined. Bauxite ore is mined in Australia. Bauxite contains aluminium oxide, iron oxides and silicon dioxide. The commercial product to be refined from this ore is aluminium.
- A **mineral** is a substance with a fixed chemical composition. A mineral is also a compound as it always has the same chemical formula. The aluminium oxide that is extracted from bauxite ore is called alumina and is a mineral with the formula Al_2O_3. Sphalerite is the mineral ZnS, zinc sulfide, from which zinc is extracted.

Figure 2.3 ▼
Ores and minerals often appear quite different: a) bauxite ore; b) alumina mineral.



Art Directors & TRIP/Alamy



Martyn F. Chillmaid/Science Photo Library

- A **by-product** is a product from a chemical process that is not the desired end product but has commercial value. For example, in the production of uranium, there is often enough gold in the ore to extract and sell.
- A **waste product** is a product from a chemical process that is toxic or dangerous or has no commercial value. It must be disposed of carefully to avoid environmental contamination.
- **Yield** is the quantity of product obtained from a chemical process. The theoretical yield is predicted from stoichiometry. The actual yield is the final quantity of the product that is obtained. Actual yield differs from theoretical yield for chemical, economic and safety reasons.

Physical processes

In Year 11, you learnt about mixtures and how the components of a mixture can be separated. A mixture contains different chemicals that often have different properties, such as boiling point, physical state, particle size and solubility. Chemists use these properties and simple physical processes to extract the desired chemicals from mixtures. A physical process does not involve a change in a chemical, but may involve a change of size, shape or state.

Crushing or grinding is a common physical process that takes place prior to chemical processes (Figure 2.4). When a substance is crushed or ground, its surface area increases, which means it has more particles available for collision during a chemical reaction and so there will be an increased rate of reaction.

To revise techniques for separating a mixture, refer to Nelson Chemistry Units 1 & 2, Chapter 2.



Mark Hope/Alamy

◀ **Figure 2.4**
Crushing of an ore on the mine site increases the surface area of the ore that is available for reaction.

To cause a change of state, processes such as evaporation, cooling and distillation are used. A mixture of liquids with different boiling points can be separated by distillation – the mixture is heated and the substances with the lowest boiling points evaporate first. As they form a gas, they can be cooled and collected, thus separating them from the mixture. A mixture of gases can be cooled so that the chemicals with the highest boiling points condense first and can be collected.

Other methods include:

- dissolving substances in water. Only substances that are water soluble will dissolve. The remaining solids can be filtered and separated
- centrifuging by spinning at high speed. This separates substances on the basis of their density.

Chemical processes

In Year 11, you learnt about chemical changes and the range of chemical reactions that can be used to convert one chemical into another. A chemical process uses chemical reactions that change the chemical composition of a substance. It can include:

- combustion reactions of fuels
- oxidation and reduction reactions in electrolysis
- roasting of chemicals in oxygen
- organic reactions to change or join functional groups.

Energy in the chemical industry

Energy is a major factor in chemical production. Most energy comes from the combustion of the fossil fuels coal, natural gas and petroleum. Chemical companies also use hydroelectricity or other renewable energy sources where available because they can be cheaper and cause less environmental damage. For example, in Australia many companies that refine metals that require electrolysis are located in Tasmania to take advantage of the hydroelectricity available there.

Energy is used in many areas in the chemical industry. The following are listed in order of increasing energy used:

- To power machines for physical processes such as crushing and grinding
- For transporting materials in trucks, on conveyor belts or in pipes
- For heating chemicals in roasting or evaporative processes such as distillation
- For electrolysis of chemicals, either of aqueous solutions or molten solutions

Figure 2.5 ▼ Energy use in the chemical industry: a) heating a chemical reaction, b) electrolysis and c) transport



RIA Novosti/Science Photo Library



ITAR-TASS Photo Agency/Alamy



Frederico Rostagno/Shutterstock.com

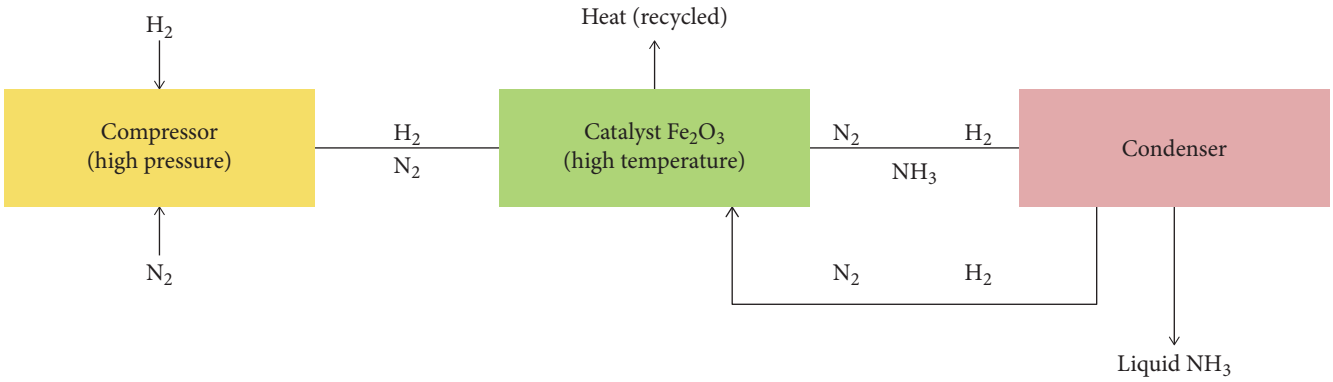
Electrolysis is a highly energy-intensive process; using machines to crush chemicals and perform simple physical processes is much less energy intensive.

Many reactions used in the production of a chemical are exothermic and so produce heat. This heat can be redirected to other parts of the production; for example, it can be used in distillation or for roasting a chemical. Catalysts also reduce the amount of heat required for a reaction. Catalysts lower the activation energy of a reaction, allowing the reaction to occur at a lower temperature than normal. Chemical industry processes are usually run 24 hours a day, 7 days a week. To stop and start machinery requires more energy than to keep it running continuously.

Flowcharts

The production of a particular chemical can be represented by a chemical flowchart. A flowchart shows each step in the production of the chemical and how the chemicals move through the chemical plant. Figure 2.6 shows a simple flowchart for the production of ammonia (NH_3).

▼ **Figure 2.6**
Flowchart of ammonia production



From a flowchart such as this, you should be able to identify the different steps in the process, raw materials used, where energy might be required, where energy might be recycled and where recycling of chemicals can occur.

The chemicals required for this process are nitrogen and hydrogen. As these are not raw materials, it is highly likely that they would need to be purchased or converted from raw materials. The gases are fed into a compressor, which puts them under pressure, resulting in a faster rate of reaction. The gases are then passed over catalysts to lower the activation energy of the reaction and increase the reaction rate without a need for extra heat. Extra heat is avoided because it lowers the equilibirum yield in this reaction.

At the end of this stage, the flowchart tells you that three chemicals continue into the process – nitrogen, hydrogen and ammonia. The reaction to form ammonia is an equilibrium reaction in which both reactants and products are present after reaction.

The reaction for the formation of ammonia is:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

This is an exothermic reaction, so heat is produced. This heat can be recycled to other parts of the plant; for example, to run machinery.

The three gases are then fed into another section where they are cooled. The higher boiling point ammonia condenses to a liquid, and the nitrogen and hydrogen remain as gases and are recycled. The ammonia has hydrogen bonding between molecules, causing the higher boiling point, while the nitrogen and hydrogen have dispersion forces between molecules, causing them to remain as gases.

The chemistry of ammonia production will be covered later in this chapter (p. 49).

ACTIVITY 2.1

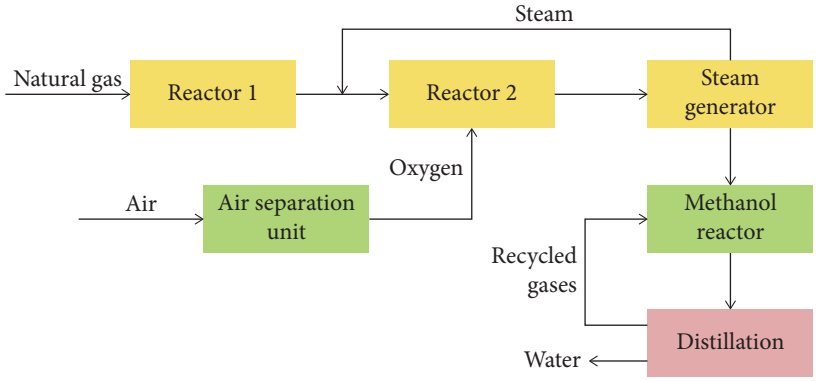
INTERPRETING A FLOWCHART

Aim

To describe the process of methanol production using the flowchart and equations provided

You will need

- Figure 2.7 showing the production of methanol and the following information:
  - In Reactor 1, the following reactions occur at 800°C and 30 atm of pressure and a nickel catalyst:
    $CH_4(g) + H_2O \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H = +208\,kJ\,mol^{-1}$
    $CO(g) + H_2O \rightleftharpoons CO_2(g) + H_2(g)$ $\Delta H = -41\,kJ\,mol^{-1}$
  - In Reactor 2, the following reaction occurs at 1000°C and 30 atm of pressure with a nickel catalyst:
    $2CH_4(g) + O_2 \rightleftharpoons 2CO(g) + 4H_2(g)$ $\Delta H = -36\,kJ\,mol^{-1}$
  - In the methanol reactor, the following reaction occurs at 350°C and 300 atm of pressure:
    $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l)$ $\Delta H = -103\,kJ\,mol^{-1}$



▲ **Figure 2.7** Flowchart of methanol production

What to do

Working alone or with another student, answer the questions to fully analyse this chemical production process.

1. Identify raw materials, waste products and by-products if they exist. Explain why you identified the chemicals as you did.
2. Explain why the step in the air separation unit is necessary.
3. Between each step (each square box), write the formulas of the chemicals that are moving between each stage.
4. Identify places where chemicals can be recycled and what gases would be recycled in the different stages.
5. Identify and explain areas of the production process that would require high energy, medium energy and low energy.
6. Identify areas where energy could be recycled.
7. Explain why catalysts are used in the production of methanol.
8. Explain why the reaction in the methanol reactor occurs at high pressure.

Metal production

Mining of metals and other minerals in Australia is a major contributor to the economy. The mining industry makes up 20 per cent of all goods and services that are produced in Australia as well as a significant proportion of exports. Mining companies contribute to the growth and infrastructure of many country towns such as Kalgoorlie and Mount Isa. Many companies provide recreation and other facilities due to the high number of workers who live in the area.

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126)

How metals are found

Very few metals are found in pure form in nature. During the Gold Rush in the 1800s in Australia, pure gold nuggets could be found lying just under the surface of Earth. But you will never find pure aluminium or zinc in the environment. Metals such as these are found as minerals, usually contained in an ore, a mixture of different minerals. This is because different metals have different activities. They react more or less vigorously with acids, water and even other metals and metal ion solutions.

Some metals such as aluminium and sodium are very active so will react with water, oxygen and any chemicals in the environment. These metals are always found as minerals. Sodium is commonly found as sodium chloride (NaCl) in seawater, while aluminium is found combined with oxygen in the form of alumina (Al_2O_3).

Gold is an unreactive metal so can be found in its pure form as it will not react with oxygen, water or other chemicals. Most metals are active enough that they will not be found in pure form. A big part of the metal production industry is the extraction of the metal from its mineral form. Pure metals are in high demand in areas such as the construction and manufacturing industries.

To learn about the activity of metals, refer to Chemistry sections 3.2 and 3.4, pages 207 and 216.

From mineral to metal – reduction processes

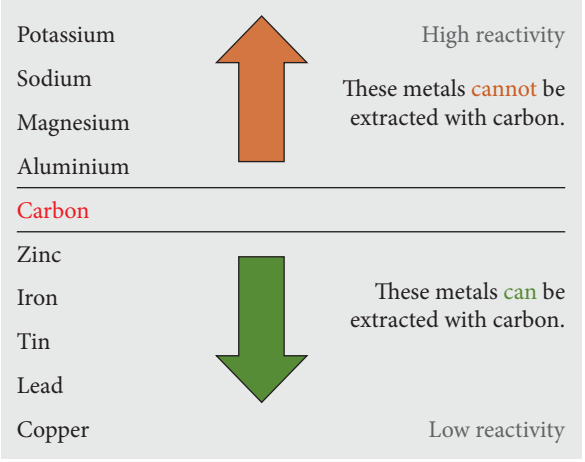
Metals are extracted from minerals and ores through a chemical process called reduction. The metals are in the mineral in ionic form and they undergo a reduction reaction to the metal. The method of reduction used is different for different metals and depends on their activity. Two common reduction methods are carbon reduction and electrolysis.

To learn about oxidation and reduction reactions, refer to Chemistry section 3.5, page 218.

Carbon reduction

Carbon has a place in the activity series, just as the metals do. You can see this in Figure 2.8. Metals that are below carbon on the activity series, such as iron, lead and copper, can theoretically be reduced by carbon. Reactive metals above carbon, such as sodium, magnesium and aluminium, cannot be reduced by carbon.

In the case of iron, carbon reduction happens in a structure called a blast furnace (Figure 2.9). The iron goes into the blast furnace in the form of iron(III) oxide (Fe_2O_3). Iron is added with coke, a form of relatively pure carbon, and limestone or calcium carbonate ($CaCO_3$).



◀ Figure 2.8
The place of carbon in the activity series

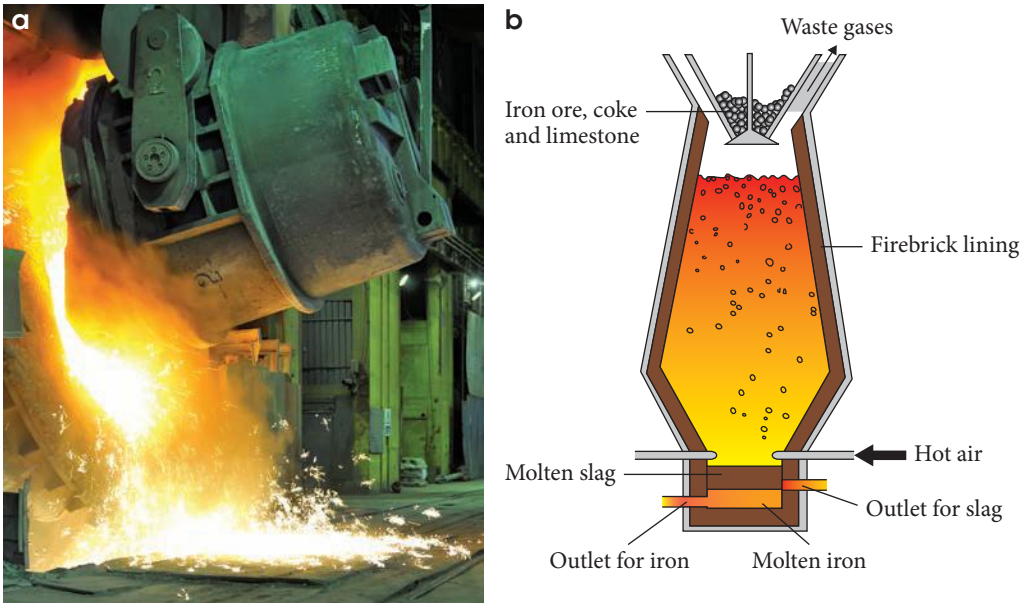


Figure 2.9 ▶ Iron is produced in a blast furnace. a) From the outside; b) what happens inside

The blast furnace is hotter at the bottom, around 1900°C, and cooler at the top, around 300°C. Hot air is blasted in at the bottom of the furnace and the oxygen reacts with the carbon to form carbon dioxide:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

This is a highly exothermic reaction so produces a large amount of heat. This is why the temperature at the bottom of the furnace is so high.

The carbon dioxide is pushed up the furnace and reacts with more carbon, forming carbon monoxide:

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

The carbon monoxide then reacts with iron(III) oxide to form iron metal and carbon dioxide:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

Because the inside of the blast furnace is so hot, the iron melts and forms a liquid at the bottom of the blast furnace. It is collected via an outlet at the bottom of the furnace.

The calcium carbonate is used to remove the silicon dioxide and aluminium oxide impurities in the iron ore that is used. The calcium carbonate first decomposes to form calcium oxide, which is a basic oxide:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

The silicon dioxide is an acidic oxide and the aluminium oxide is an amphoteric oxide, so both will react with the basic calcium oxide to form calcium silicate and calcium aluminate:

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$CaO + Al_2O_3 \rightarrow Ca(AlO_2)_2$$

These two products form a substance called slag that floats on top of the molten iron because they are less dense. The slag will eventually solidify and have a glassy appearance due to the silicates present.

To learn about the process of electrolysis, refer to Chemistry section 5.6, page 266.

Electrolysis

Some metals can be reduced by carbon but in industry are normally reduced through the process of electrolysis. Zinc is such a metal. While it is possible to reduce zinc in a blast furnace, in industry an aqueous solution of zinc sulfate is electrolysed to produce zinc in commercial quantities. The reasons for this are economic. The high reactivity of zinc makes it difficult to reduce by carbon and more

heat is required than for metals such as iron and copper. Electrolysis is a more efficient method when considering the cost of energy required for the reduction to the zinc metal.

Reactive metals such as sodium and magnesium cannot be reduced by carbon reduction. Electrolysis must be used to reduce the metal ions to the solid metal.

An aqueous solution of zinc undergoes electrolysis with a lead anode and an aluminium cathode as seen in Figure 2.10. At the cathode, the zinc is reduced from zinc ions to zinc metal:

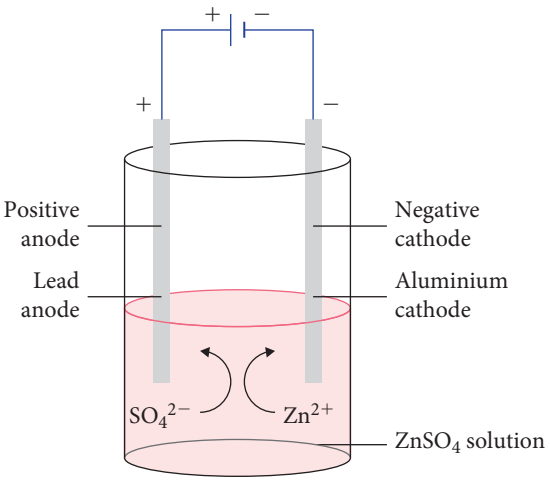
$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$

The solid zinc plates onto the aluminium cathode. It is scraped off periodically and recovered. The zinc produced is about 99.95 per cent pure and does not need the last stage of metal production, refining.

At the anode, water oxidises to form oxygen gas and hydrogen ions:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

The hydrogen ions combine with the un-reacted sulfate ions to form sulfuric acid, which is recycled into the process to react with the zinc oxide in the preparation for the reduction stage.



▲ **Figure 2.10**
A simple zinc reduction electrolytic cell



Ria Novosti/Science Photo Library

▲ **Figure 2.11**
A zinc electrolytic plant

The reduction stage of aluminium uses electrolysis like zinc does; however, the aluminium oxide must not be an aqueous solution. The desired reaction for the reduction of aluminium at the cathode is:

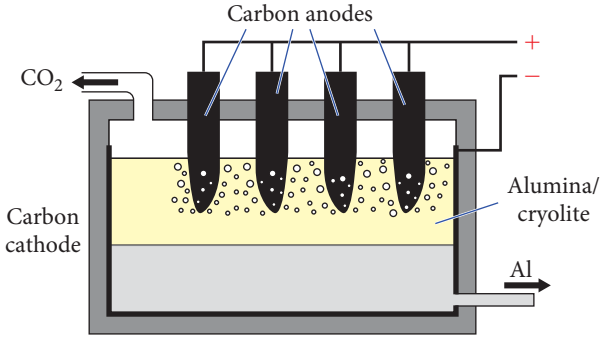
$$Al^{3+} + 3e^- \rightarrow Al(s)$$

If an aqueous solution of aluminium ions is used, instead of aluminium metal, the following reaction happens at the cathode:

$$2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$$

This is related to the position of aluminium on the metal activity series. If water is present, then it will be reduced in preference to reactive metals such as aluminium and sodium. Metals above zinc, such as aluminium, lithium and sodium, must be produced using molten salt electrolysis as they will not be reduced to the metal if water is present.

The production of aluminium by molten salt electrolysis uses the set-up seen in Figure 2.12. The carbon anodes of the cell are dipped into a mixture of alumina and cryolite. Pure alumina (Al_2O_3) is not used because it has a melting point of 2030°C.



▲ **Figure 2.12**
Electrolysis of molten aluminium ions

The amount of energy needed to keep the alumina molten is extremely high and costs the company a lot of money. To reduce the costs involved with this process, a mixture of alumina with cryolite (Na_3AlF_6), calcium fluoride and aluminium fluoride

is used. This mixture has a melting point of 940–980°C, around half that of the pure alumina. This reduces costs significantly and makes for a more efficient and economically viable metal production process.

The cathode is the carbon lining of the container in which electrolysis occurs. At the cathode, the aluminium ions are reduced to aluminium, which forms a molten metal that is released out of the base of the container:

$$Al^{3+}(aq) + 3e^- \rightarrow Al(l)$$

At the anode, oxygen ions oxidise to form oxygen gas:

$$2O^{2-}(aq) \rightarrow O_2(g) + 4e^-$$

This oxygen gas reacts with the carbon anodes to form carbon dioxide, gradually eating the anodes away. The carbon anodes are replaced periodically as they lose mass.

In Australia, the mining of aluminium and electrolytic refining do not occur in the same place due to the huge energy costs associated with this refining. The mining and initial chemical refining of the aluminium ore takes place in Western Australia, the Northern Territory and northern Queensland. The electrolytic refining needs to take advantage of low-cost energy sources. In Tasmania, there is access to electricity that is generated by hydroelectric methods, providing cheaper electricity than fossil fuel-powered stations. Bell Bay in northern Tasmania is the location for a number of metal refining plants for this reason.

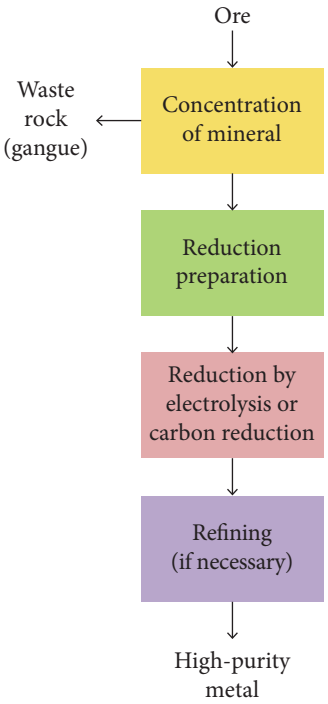


Figure 2.13 ▲ Stages of metal production

Stages in metal production

The reduction of the metal is only one stage in the overall production of metals. A number of processes occur both before and after reduction including purification and refining. All metal production follows the same basic stages, which are shown in Figure 2.13.

The first stage of metal production is to concentrate the ore. Some ores when they are mined are very concentrated already. When iron ores are mined, they are usually around 50 per cent iron mineral, so they do not need to be concentrated. Zinc ores are only around 8 per cent zinc mineral, so must be further concentrated before the next stages are completed.

The second stage is to prepare the concentrated mineral for reduction. The aluminium oxide mineral must have all water removed prior to reduction so this stage involves a process called calcining, which removes all water from the alumina mineral.

The third stage is reduction from the mineral to the metal by electrolysis or carbon reduction. Electrolysis can be with either an aqueous solution or a molten chemical for highly active metals. Carbon reduction can be used for less active metals.

The fourth and final stage is the refining of the metal. After electrolysis or carbon reduction, metals such as zinc and aluminium may be pure enough to use immediately. Other metals, such as copper, need further refining to be useful. The copper obtained from reduction is 98–99 per cent pure, but needs to be 99.90 per cent pure for use in copper wiring.

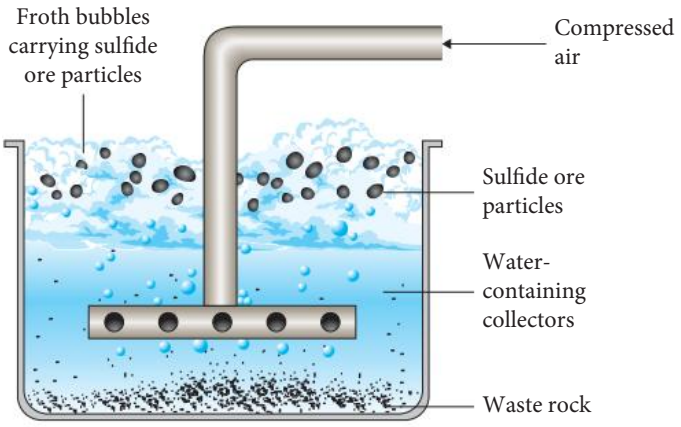
Zinc production

Zinc metal is in high demand as an anticorrosion agent. Covering another metal with zinc – galvanising – is one of the most popular ways of protecting iron and steel from corrosion. Zinc makes up about 0.0075 per cent of Earth's crust, mostly as a sulfide mineral. The most common zinc mineral is sphalerite, zinc sulfide (ZnS). Other minerals present in the ore include iron, copper and lead sulfides.

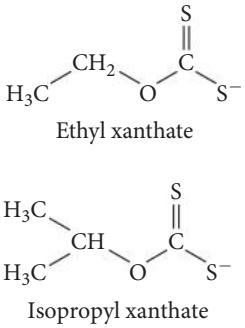
Concentration by froth flotation

The first stage in the concentration of zinc sulfide ore is to crush and grind the ore in order to separate the mineral grains from the waste grains. The mineral grains then have a surface active agent added and are 'floated' from the waste and separated using bubbles of air. See Figures 2.16 and 2.17.

Froth flotation is an Australian invention from the end of the 19th century. At this time, metal prices had fallen so mining companies could not make a profit from extracting metals from waste rock. Guillaume Delprat, a Spanish migrant to Australia, was an engineer



▲ Figure 2.14
Set-up for froth flotation



▲ Figure 2.15
Xanthate ions

with Broken Hill Proprietary (BHP). He developed the process of froth flotation that was so successful at processing waste rock that within 10 years nearly 6 million tonnes of waste had been processed, producing zinc valued at $60 million, a lot of money in the late 1800s. His method was so efficient that it was adopted by mining companies worldwide and is still used today.

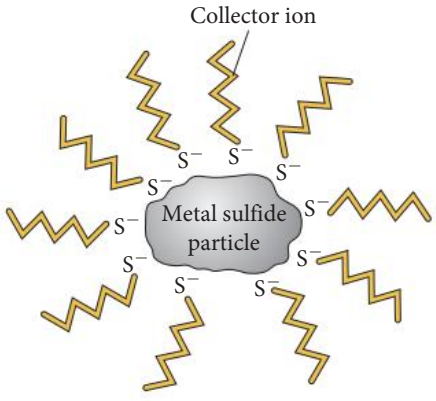
Froth flotation is a concentration method that uses a large tank full of water. The zinc ore powder is added to the water along with a frothing agent and chemicals called collectors. The tank and chemicals used in froth flotation can be seen in Figure 2.14.

Collector molecules have a polar ionic and a non-polar end. Common collectors are the ethyl xanthate ion and the isopropyl xanthate ion (Figure 2.15). Both structures have a charged ionic region and a non-polar hydrocarbon-based region. This allows the xanthate ions to bond to an ionic surface. As the hydrophobic (non-polar) tails face outwards, these will attach to air bubbles and the grain is floated to the surface.

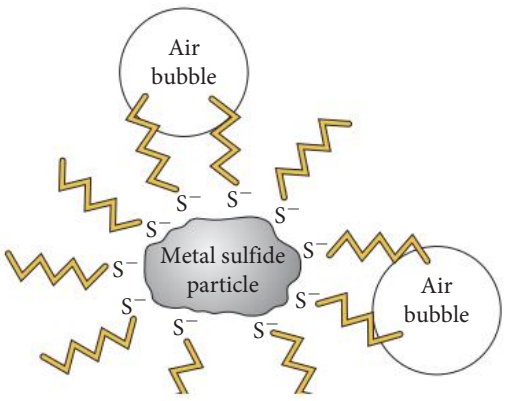
The ionic region bonds to the positive zinc ions of the zinc sulfide ore, as seen in Figure 2.16. Multiple xanthate ions attach to the zinc sulfide grains and surround them. The non-polar regions all face outwards, making the whole structure non-polar.

Air is then blown into this mixture. The non-polar nitrogen and oxygen molecules in the air bond with the non-polar region of the xanthate ions, as shown in Figure 2.17. The air bubbles rise and form a froth of zinc sulfide ore at the top of the tank as seen in Figure 2.18. At this stage, the zinc sulfide has concentrated to about 30 per cent, up from 8 per cent in the initial ore.

To collect different minerals in other metal production, different collectors are used. Each collector is capable of forming this froth with different minerals. The collectors used for zinc sulfide froth flotation do not bond to the lead sulfide or iron sulfide grains in the powdered ore. The lead and iron in the ore are thus separated from the zinc in this manner.



▲ Figure 2.16
Xanthate ions attached to a grain of zinc sulfide



▲ Figure 2.17
Air bubbles attached to the xanthate ion–zinc sulfide structure

ORESOME FROTH

Complete this interactive activity, which lets you adjust froth flotation conditions and measure the outcome.



age fotostock/Alamy

Figure 2.18 ▲
The zinc sulfide froth on the top of the tank

Preparation for electrolytic reduction

The zinc sulfide is collected and washed, then roasted in air. During this process, the zinc sulfide reacts with oxygen to form zinc oxide:

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

Sulfur dioxide is a product of this reaction. The release of sulfur dioxide into the atmosphere can cause acid rain to form. This will be discussed further on page 47.

Zinc oxide (ZnO) is unsuitable for the electrolytic reduction to form zinc metal. Sulfuric acid is added to the zinc oxide to form zinc sulfate ($ZnSO_4$) solution in the reaction below:

$$ZnO(s) + H_2SO_4(aq) \rightarrow ZnSO_4(s) + H_2O(l)$$

This zinc sulfate solution often contains less active metal ions such as cadmium ions (Cd^{2+}), copper ions (Cu^{2+}) or silver ions (Ag^+). Powdered zinc dust is added to the zinc sulfate solution. Less active metals will be displaced by the solid zinc as seen in the following reaction:

$$2Ag^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$

The solid metals that form from this reaction can be filtered from the solution prior to electrolysis. It is important that these less active metals are removed. If they are present during the electrolysis, then they will reduce to the solid metal in preference to zinc ions as they are less active. This will result in impure zinc being produced.

Production of other metals

Other metals such as iron, copper and aluminium are widely used because of their specific properties. Copper is highly conductive, iron is strong when alloyed to make steel and aluminium is light and flexible.

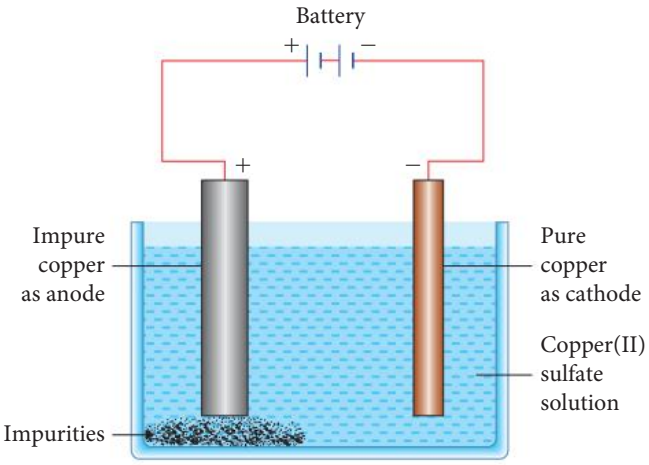
As described earlier, the production of metals follows four basic stages. Table 2.1 shows some of the similarities and differences in the production of these four important metals.

Table 2.1 Comparing the production of zinc, copper, iron and aluminium

	Zinc	Copper	Iron	Aluminium
Mineral and ore composition	Sphalerite (ZnS) around 8%	Chalcopyrite ($CuFeS_2$) or cuprite (Cu_2S) around 5%	Haematite (Fe_2O_3) or goethite ($Fe_2O_3.H_2O$) around 70%	Bauxite ($Al_2O_3.3H_2O$) up to 30%
Concentration of the metal	Froth flotation to about 30%	Froth flotation to about 30%	Not required	Chemical leaching process to more than 35%
Preparation for reduction	Roasting and conversion to zinc sulfate	Smelting resulting in an increase in concentration to 40–50%	Sintering	Removal of water ready for molten electrolysis
Reduction	Aqueous electrolysis to produce 99.95% pure zinc	Reduction by carbon or roasting in oxygen to produce 98–99% pure blister copper	Reduction in a blast furnace using carbon to produce pig iron of 80–95% purity	Electrolysis of molten aluminium oxide to produce 99.3–99.6% pure aluminium
Refining	Not required	Electrolysis to produce 99.99% pure copper	Removal of carbon and alloying with other metals to create steel	Not required

Further refining of metals

After the reduction stage, copper metal is not pure enough for use as an electrical conductor. After reduction, it is 98–99 per cent pure and referred to as blister copper. Impurities such as silver and gold are still present in the copper metal. Electrolytic refining is used to purify the copper to 99.90 per cent purity. The set-up for the refining can be seen in Figure 2.19.



◀ **Figure 2.19**
Electrolytic refining of copper metal

The impure blister copper is the anode. As it oxidises, the copper metal forms copper(II) ions while the silver and gold in the metal do not oxidise and fall to the bottom of the tank. The copper(II) ions that form reduce onto a very thin sheet of pure copper used as the cathode. The reactions are:

- Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
- Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

The cathode is extremely pure copper and increases in mass. It is replaced periodically with another thin sheet. When the impure blister copper at the anode is used up, it is replaced by another anode of blister copper to be purified.

MINING AND REFINING OF ALUMINIUM

View this interactive flowchart of aluminium production in Australia.

ACTIVITY 2.2

PRODUCTION OF OTHER METALS

Aim

To investigate the full production of a metal other than zinc

What to do

1. Working individually, in pairs or in small groups, choose a metal to investigate. Use the internet and textbooks to describe how it is produced in the four stages.
2. Make a poster or a flowchart of the process. Include diagrams and equations in your descriptions.

What did you discover?

1. Explain the steps of the production of your metal using chemical theory you have studied. You could refer to reaction rates, equilibrium, electrochemistry or other areas that are applicable to your metal production process.
2. Compare this metal production process to that of zinc and identify similarities and differences in the production process.
3. Compare your metal to those of other students. Identify similarities and differences between different metal production processes.

Testing metals for purity

Most uses for metals are as alloys in which other elements are mixed into the metal lattice to give it useful properties. An alloy you would be familiar with is stainless steel, which is iron that contains at least 10 per cent chromium. This gives the steel excellent corrosion-resistance properties.

It is almost impossible to produce a perfectly pure metal, but some metals are required to have exceptionally high purity. Copper wiring has improved conductivity with increased purity. Copper used in electrical wiring is 99.90 per cent pure copper.

Gold jewellery is valued on the basis of its purity. The unit for purity of gold alloys is the karat, with symbol kt. Karat purity is measured as follows.

$$\text{Karat rating} = 24\frac{\text{mass of gold present}}{\text{total mass of material}}$$

24-karat gold is regarded as '100 per cent' pure. 24-karat gold is actually only 99.9 per cent pure but is as close as gold will become. 18-karat gold is 18 parts gold and 6 parts other metals, whereas 12-karat gold is 12 parts gold and 12 parts other metals. The more gold that is present, the more expensive the jewellery.

Figure 2.20 ▼
Pure metals and their uses: a) 24-karat gold jewellery; b) copper wiring

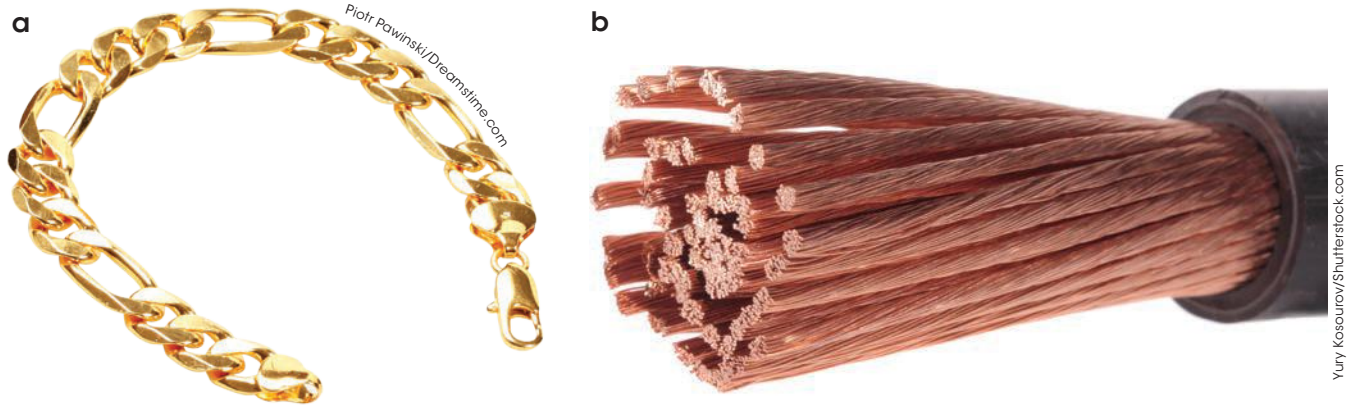


Figure 2.21 ▼
Fire assay showing the gold bead that forms after heating

A metallurgical assay is the analysis of a metal, an alloy or an ore to determine its exact composition. A variety of methods are used.


Arrakis, Incorporated – Englewood, CO. Photographer – Michelle Hite

Assaying

A fire assay is an accurate method of measuring purity involving the chemical conversion of the ore or metal sample by exposure to high levels of heat. Gold purity can be measured to 1 part in 10 000 while detection of metals in an ore can be as sensitive as 1 part per billion. While incredibly accurate, it does result in the destruction of the sample during the process, which is not always possible.

To complete the assay, the gold alloy is mixed with high-purity lead and silver in a specially designed crucible called a cupella. The crucible absorbs non-precious metal oxides, leaving the gold to form a pure gold bead. This bead is weighed to accurately measure the amount of gold in the alloy. Other metals are absorbed by the crucible so they do not interfere with the measurement of the gold.

Atomic absorption spectroscopy

To revise AAS, refer to Nelson Chemistry Units 1 & 2, Chemistry section 1.10, page 131.

Atomic absorption spectroscopy (AAS) is a method of analysis that atomises a sample, and uses absorption of light to measure the quantity of an element present. Testing for a particular element involves using a cathode lamp of the metal or element being tested. The amount of light absorbed by the sample is an indication of the concentration of that element in the sample.

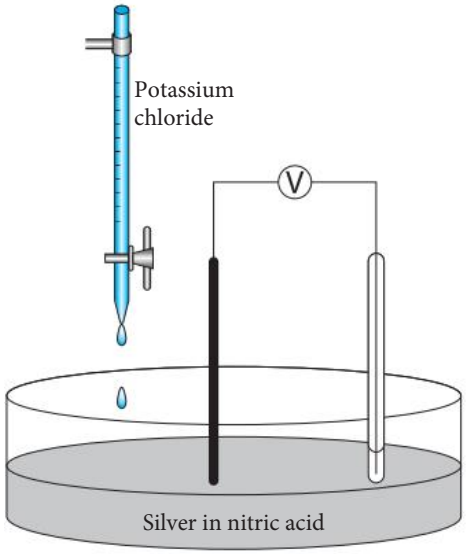
In the mining industry, AAS is used to measure the concentration of metals in an alloy as a purity test. As described earlier, the purity of a metal is important, and all metals are tested prior to sale to ensure they meet the standards required.

Titrations

A type of titration called a potentiometric titration is used to determine the purity of silver, gold and palladium.

In this type of titration, there is no need for an indicator. Instead of using a chemical to determine the endpoint, the electric potential across the solution is measured. Ions in a solution are conductive; the more ions that are present, the higher the conductivity of the solution. Two electrodes are placed into the solution to measure the potential across the solution, as seen in Figure 2.22.

▼ **Figure 2.22**
Set-up for a potentiometric titration



To measure the amount of silver in an alloy, the silver sample is weighed, and then dissolved in nitric acid to form a silver nitrate solution. Potassium chloride solution is added via a burette, causing the silver ions to precipitate as silver chloride.

The endpoint of the titration is detected through a set of electrodes that measure the changes in the electrical conductivity of the solution due to the silver ions. As the silver ions precipitate, the conductivity decreases as fewer ions are present.

The amount of potassium chloride that was required to cause all the silver to precipitate is then used to calculate the mass of silver in the solution. This is compared to the mass of the original silver alloy sample and a percentage of silver in the sample is calculated.

Environmental issues with metal production

The production of metals has a number of negative environmental issues associated with it. Two major issues come from the production of carbon dioxide through use of fossil fuels and the production of waste products such as sulfur dioxide that contribute to acid rain.



To learn about volumetric analysis and titrations, refer to Chemistry sections 4.2 and 4.4, pages 226 and 234.

Enhanced greenhouse effect

As described earlier, the production of metals is very energy intensive. The use of fossil fuels to heat and roast chemicals, to provide electricity for electrolysis and to keep electrolytes molten, results in the production of large amounts of carbon dioxide. Carbon dioxide is a greenhouse gas so it absorbs infrared radiation in the atmosphere. Carbon dioxide produced through fossil fuel combustion is a major contributor to the **enhanced greenhouse effect**.

The increase in carbon dioxide in the atmosphere in the last 50 years is undeniable. Measurements taken by the US National Oceanic and Atmospheric Administration (NOAA) at the Mauna Loa Observatory in Hawaii show a steady increase in the amount of carbon dioxide in the atmosphere.

People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk. (ACSCH085 and ACSCH123) AC

Science can be limited in its ability to provide definitive answers to public debate; there may be insufficient reliable data available, or interpretation of the data may be open to question. (ACSCH086 and ACSCH124)

International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region. (ACSCH087 and ACSCH125)

Carbon dioxide absorbs infrared radiation, so this increase in carbon dioxide means an increase in the amount of heat that is trapped in the atmosphere. The most obvious consequence of this extra heat is a rise in global temperatures. The effects of this are already being seen in various parts of the world.

However, there is controversy about these effects. Some scientists have expressed concern over the interpretation of the data that has been collected and think that the predicted effects and temperature increases have been exaggerated.

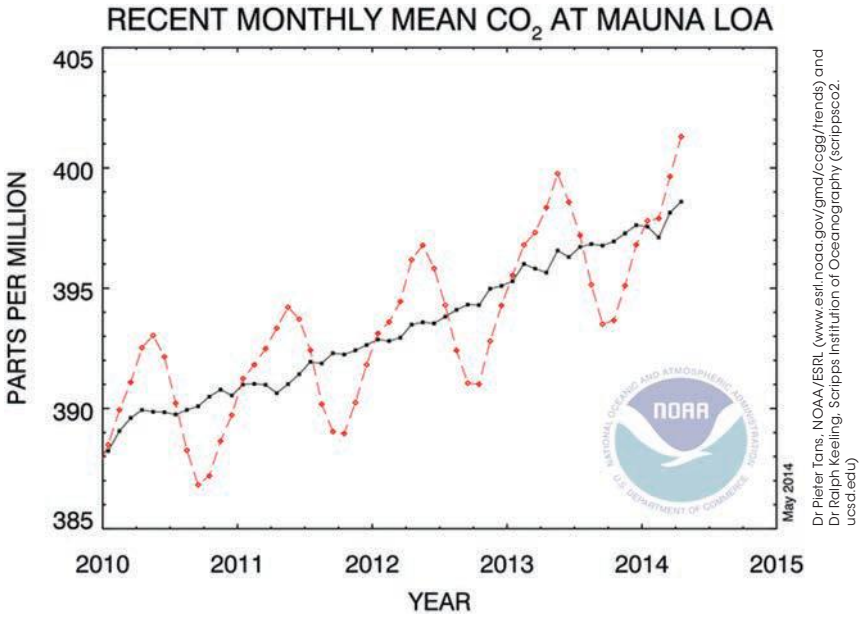


Figure 2.23 ▶ Concentrations of carbon dioxide measured in Hawaii by NOAA

Consequences of enhanced greenhouse effect

Glaciers in the Arctic and other areas have experienced significant shrinkage; ice formation in the far north and south of the planet occurs later in winter and starts to break up earlier in spring than ever before. There is recorded loss of sea ice in the Arctic; sea levels have risen, which in the long term could result in land loss and flooding of coastal cities.

Other effects are harder to link definitively to an increase in carbon dioxide and global temperatures. However, there is no doubt that we are seeing prolonged heat waves and droughts in summer and more severe snowstorms in winter. Hurricanes, severe storms and cyclones have increased in frequency and intensity.

Dealing with the problem

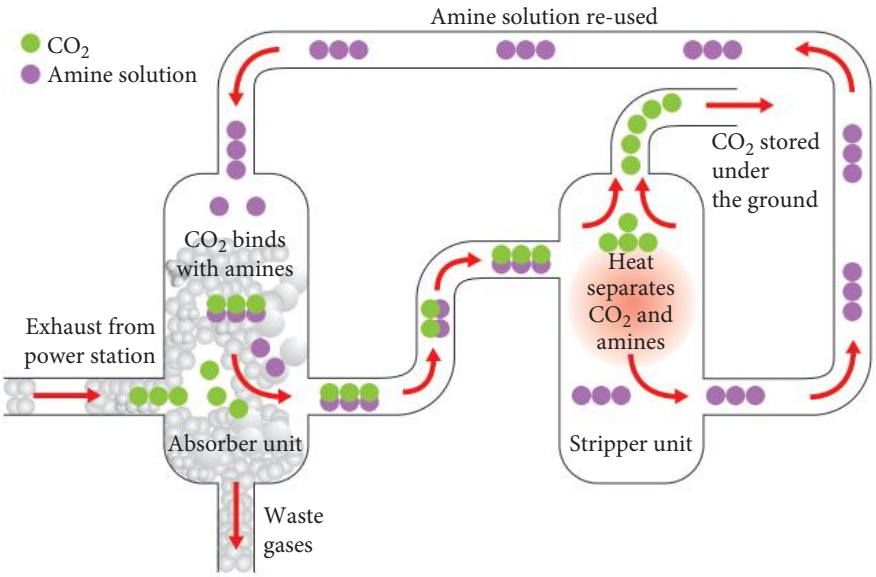
There are a number of ways of dealing with the emission of carbon dioxide during combustion. Coal-fired power stations currently produce 40 per cent of Australia's greenhouse gas emissions. One way of reducing the amount of carbon dioxide emitted is post-combustion capture. This method is already widely in use in the oil, gas and chemical industries.

CSIRO in Australia is a world leader in the development of this technology. They have collaborated with scientists and energy companies in Australia and China to construct post-combustion capture plants in both countries to investigate its effectiveness and continue to improve the methods used.

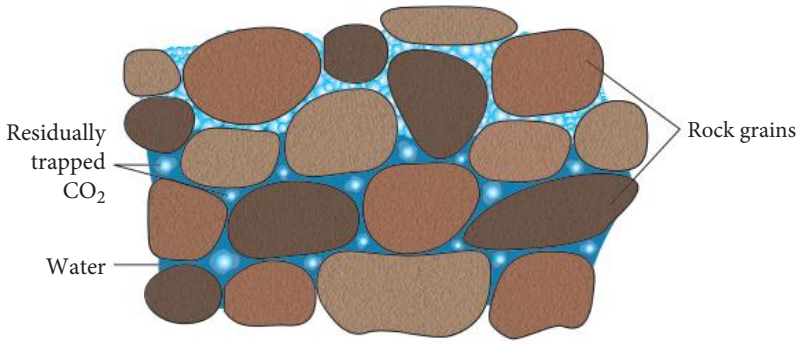
Normally in a coal-fired power station, the gases are vented to the atmosphere with around 10–15 per cent carbon dioxide present. These gases can instead be passed into a carbon dioxide absorber before release so that there is a reduction in up to 85 per cent of the carbon dioxide in the gases to be released.

The absorber is a liquid such as an amine that captures the carbon dioxide. Once the carbon dioxide is removed from the gases, the absorber is cleaned by removal of the carbon dioxide so the amine liquid can be re-used. The carbon dioxide is then converted to a liquid through cooling and compression and is geologically stored. The process can be seen in Figure 2.24.

Geological storage of carbon dioxide occurs in Australia in a number of electricity plants in New South Wales, Victoria and Queensland. The companies, in collaboration with government and scientific organisations, are conducting trials to measure efficiency and improve the methods used. Liquid carbon dioxide from post-combustion capture is pumped underground into sandstone rock. This rock is porous, meaning it has spaces in the rock where the liquid can be stored. The porous sandstone is surrounded by a non-porous rock, which seals the liquid in the sandstone so it cannot escape.



◀ **Figure 2.24**
Process of post-combustion carbon capture



◀ **Figure 2.25**
Carbon dioxide liquid stored in rock



LOW-EMISSION ENERGY FUTURE

Explore this interactive activity to find out about low-emission energy technologies.

Acid rain

Many metals are refined from sulfide minerals, such as zinc sulfide and copper sulfide. During the refining process, sulfur is removed from the mineral, often by roasting with oxygen. The product that forms is sulfur dioxide. The reaction below shows the formation of sulfur dioxide from zinc sulfide.

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

If this sulfur dioxide is released into the atmosphere, then a series of reactions occurs that forms two acids. First, the sulfur dioxide can react with water to form sulfurous acid:

$$SO_2 + H_2O \rightarrow H_2SO_3$$

The sulfur dioxide can also react with oxygen in the air to form sulfur trioxide:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

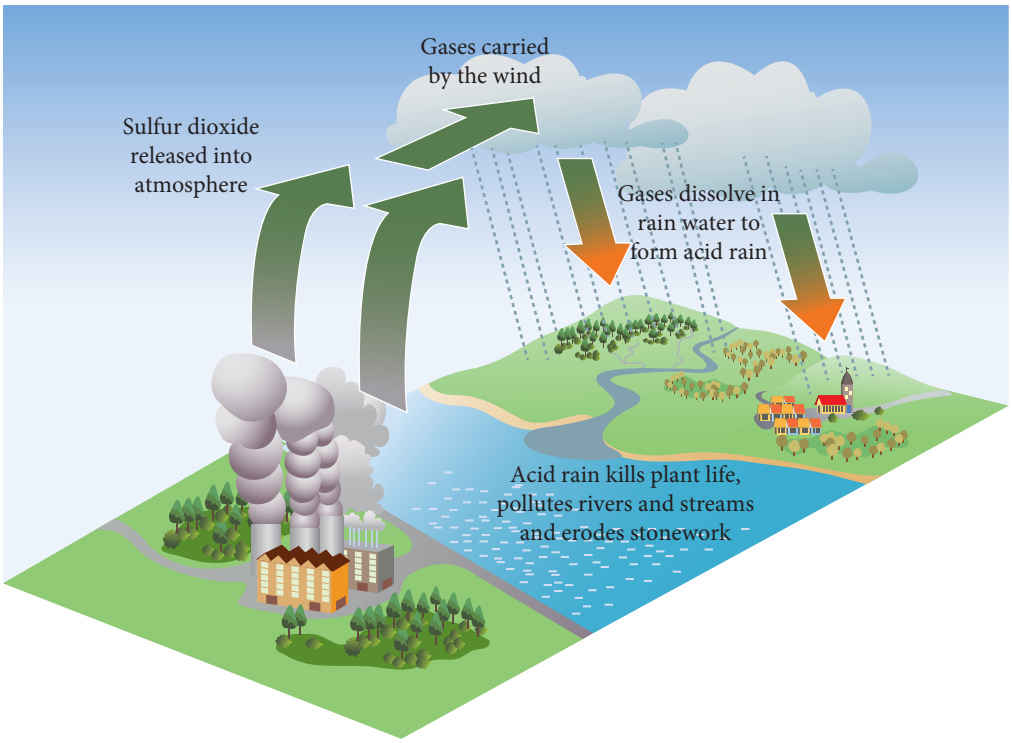
The sulfur trioxide can then react with water in the atmosphere to form sulfuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

The two acids that form have different properties. Sulfurous acid is a weak acid, so it only partially ionises and does not make a big contribution to acid rain. Sulfuric acid is a strong acid and almost fully ionises to form hydrogen ions. Sulfuric acid is most responsible for acid rain of the two acids produced.

In zinc production, the sulfur dioxide collected is a useful by-product. It is used to make the sulfuric acid that is used later in the process to make zinc sulfate. The main method of making sulfuric acid is called the contact process and is covered in detail on page 53.

Figure 2.26 ▶
Acid rain formation and some of its effects





To revise the information on acids and calculation of pH, refer to Chemistry sections 2.1 and 2.2, pages 172 and 180.

Consequences of acid rain

When acid rain falls, it can have large impacts on both the built and natural environments. One of the biggest problems occurs in the aquatic environment. Acid rain makes its way into rivers, lakes and other waterways through draining systems and run-off from the land. Lakes and rivers can become acidic, which has consequences for the aquatic life they contain.

Many soils contain negatively charged silicate ions. These bind to ions in the soil. Some of these ions are useful, such as magnesium and potassium, but others are harmful, such as aluminium. When acid rain falls, the hydrogen ions in the rain displace the ions from the soil silicates and the harmful ions are free to wash into waterways.

Low pH and aluminium ions in waterways have many negative effects. Some plants and animals can tolerate acidic conditions, but many are sensitive to changes in pH. The eggs and young of aquatic animals are particularly sensitive to low pH and the presence of aluminium ions. At a pH 5 or less, fish eggs will not hatch. If the pH is lower than this, adult fish are directly affected and will die.

Crustaceans with calcium carbonate shells are affected by acid levels because the acid reacts with the calcium carbonate to soften and potentially destroy their shells, leaving them defenceless. The chemical reaction for this is:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2$$

Ecosystems are affected when some organisms die off. Animals that rely on these organisms for food suffer, and these effects continue through all organisms in the surrounding ecosystem.

Acid rain also affects trees. Growth rates slow, leaves turn brown and photosynthesis stops. The acid in the soil releases toxic ions such as aluminium, as described above. Aluminium affects tree growth by blocking the uptake of nutrients through the roots. In severe cases, entire areas of forest in Europe and North and South America have died off due to the falling of acid rain in those areas. You can see this in Figure 2.27.

Built structures are also affected. Limestone and marble buildings in Europe have been severely affected from decades of acid rain falling. Just like crustacean shells, the calcium carbonate of limestone and marble dissolves as the acid rain falls. You can see the effects of this on a statue in Figure 2.28.



blickwinkel/Alamy

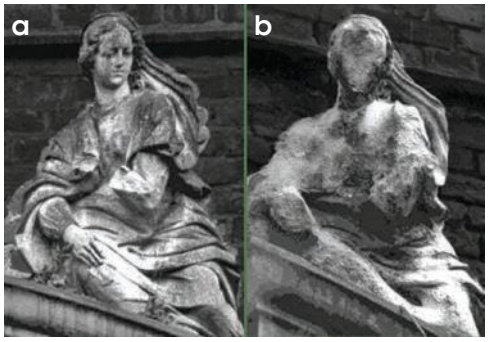
▲ **Figure 2.27**
Damage to trees due to acid rain

Fertiliser production

Fertilisers are used to replace nutrients in the soil that are taken up by plants. Large-scale growing of agricultural crops has led to increased demand for fertiliser. Chemists design fertilisers for particular soils and to suit the type of crop that is being grown. Different plants require nutrients at different levels. Soils can be acidic or alkaline and require different fertilisers that can tolerate the pH of the soil.

Fertilisers are primarily nitrogen, phosphorus and potassium based. Nitrogen is used in plants to synthesise proteins, nucleic acids and chlorophyll. It also promotes root development and leaf growth. Phosphorus is essential to regulate leaf growth and in the formation of the energy molecules ATP and ADP (adenosine triphosphate and adenosine diphosphate). Potassium is used in protein synthesis and helps with regulation of plant growth.

These nutrients can be found in naturally occurring substances such as seaweed, bones, guano (bird droppings) and phosphate rock. In the past, these types of substances were used to manufacture fertiliser, but they are not suitable for large, industrial-scale production methods. These days, many fertilisers are synthesised from raw materials such as ammonia, nitric acid and ammonium phosphate.



Herr Schmidt-Thomsen

▲ **Figure 2.28**
This sandstone figure over the portal of a castle in Westphalia, Germany, was photographed in a) 1908 and b) 1968. Acid rain accounts for the severe damage.

Haber process – production of ammonia

At the start of this chapter you looked at the flowchart for the production of ammonia, examining it for the raw materials, waste products and recycling of energy in the process. The **Haber process** is the main method for the production of nitrogen-based fertilisers. It was developed in 1915 and involves the addition of nitrogen and hydrogen to form ammonia. The ammonia produced is then used as a feedstock for the production of fertilisers. An industrial plant can produce around 1000 tonnes of ammonia a day. To produce chemicals at this level, chemists have worked to make the reactions as efficient as possible while making as much profit as they can.

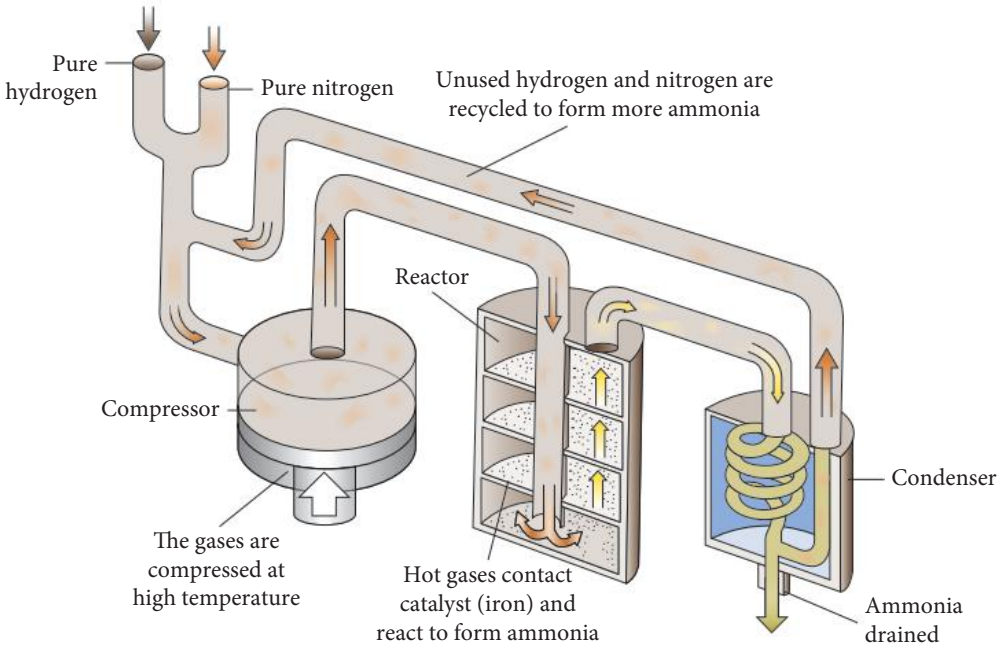
A diagram showing the equipment and method used in the Haber process can be seen in Figure 2.29.

To produce ammonia, nitrogen and hydrogen gases are reacted together in the presence of a catalyst, at a temperature of 400°C and a pressure of 250 atm. The exothermic equilibrium reaction equation is:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126)

Figure 2.29 ▶
The industrial production of ammonia





To learn about equilibrium and the effect of changes to an equilibrium system, refer to Chemistry sections 1.2, 1.3 and 1.4, pages 143, 146 and 154.

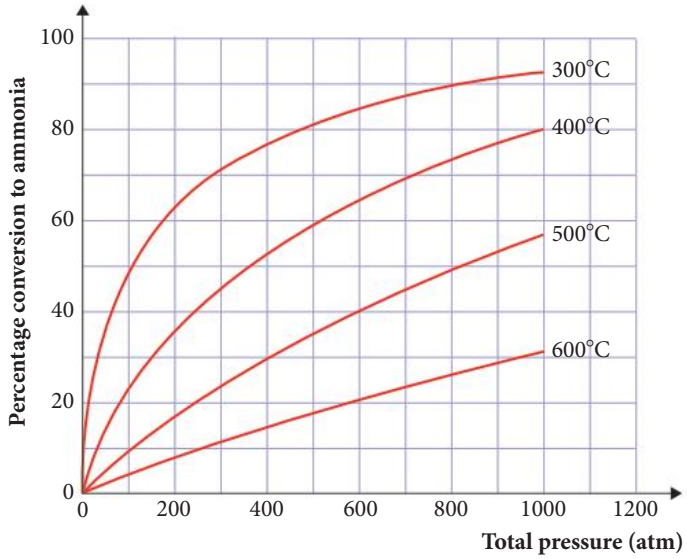
Nitrogen is sourced from the atmosphere, while the hydrogen is usually gained from methane. The methane undergoes a steam re-forming, which extracts the hydrogen from the methane for use in the Haber process. The nitrogen and hydrogen gases are fed into a compressor to increase the concentration of the gases and thus the reaction rate.

The gases are passed over beds of iron catalysts. The catalyst lowers the activation energy required for this reaction and thus increases the rate of formation of ammonia. As the gases pass over the catalyst, only about 15 per cent of the gases are converted to ammonia. The remaining gases are cooled, and fed back over the catalyst beds. Due to this recycling, around 97 per cent of the nitrogen and hydrogen is eventually converted to ammonia.

The gas mixture of ammonia and any unreacted nitrogen and hydrogen passes into a condenser, where it is cooled. The ammonia has the highest boiling point so is condensed first, leaving the nitrogen and hydrogen gases to be fed back into the reactor for further conversion.

The conditions that suit this reaction best are a medium temperature of around 400°C and moderately high pressure. As you can see in Figure 2.30, the percentage yield of ammonia is higher at lower temperatures and higher pressures. This can be explained by looking at the chemistry.

Figure 2.30 ▶
Production of ammonia at different temperatures and pressures



You have already learnt that reaction rates are improved when the temperature of the reaction mixture is increased. Extra energy for the particles results in more productive collisions and production of more chemical per unit time. A slow reaction rate is not economic or efficient for a chemical company trying to make a profit.

The reaction to form ammonia is an exothermic equilibrium reaction. Le Chatelier's principle tells us that when an exothermic reaction has energy added, the system will move to counteract the change by moving in the endothermic direction. This will absorb the added energy. But it will drive the reaction in the reverse direction, decreasing the yield of ammonia.

This is a problem that is commonly encountered in industry. An increase of heat increases the reaction rate, but decreases the yield. So what is the answer? In Figure 2.30 you can see that the yield increases as the temperature decreases, so chemists need to decide on a balance point between reaction rate and yield. What temperature gives a suitable yield of ammonia, at an acceptable rate of reaction?

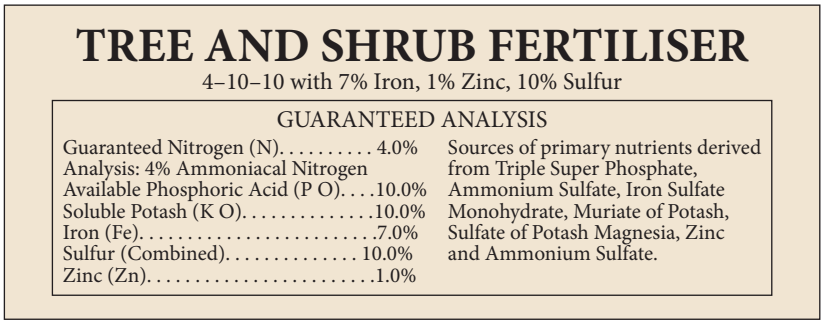
The temperature used is 400°C, high enough to maintain a suitably fast reaction rate, but not so high as to decrease the yield of the ammonia.

Another consideration in an equilibrium reaction is the pressure used. Again, Le Chatelier's principle tells us that use of high pressure will favour the forward reaction as there are fewer molecules on the right-hand side. Increasing pressure will drive the reaction to the side of fewer molecules, increasing the yield of ammonia.

The actual pressure used is 250 atm. Higher pressure would give a higher yield, but economic and safety factors must be considered. Use of higher pressure means all piping and reaction vessels used must be made of stronger material to withstand this pressure. Maintaining gases at high pressure requires use of pumps and compressors, which require more electricity to be run. This increases the costs to the company, which will reduce the profit made.

Testing fertiliser purity

Fertilisers are labelled with an NPK analysis that shows the levels of nitrogen (N), phosphorus (P) and potassium (K). The N value is the percentage of nitrogen as an element by weight in the fertiliser. The P and K values are slightly different. The values for these elements represent the amount of oxide that would be present if the phosphorus and potassium in the fertiliser were to be converted to an oxide.



◀ **Figure 2.31**
Label showing the NPK ratio on a commercial fertiliser

In the agricultural industry, it is important that the right fertilisers are used due to the size and scale of the farms involved. Use of the wrong fertilisers can be costly to a farmer as crop growth is affected, reducing profits. Analysis of fertilisers and correct labelling is important because it provides information to both the agricultural industry and household users.

Gravimetric methods

A common method of analysing the composition of fertilisers is gravimetric analysis. The fertiliser is dissolved in water, and then chemicals are added to precipitate the substance to be analysed. The solid precipitate is filtered from the solution, weighed and compared to the mass of the initial mass of the fertiliser. From this, a percentage composition of an element or compound can be determined.

An example of this is determination of sulfate content in lawn fertilisers. Sulfur is an important plant nutrient often found in fertilisers as ammonium sulfate. This chemical is suitable for use in alkaline soils as it helps to lower the acidity of the soil, promoting better plant growth.

The fertiliser containing ammonium sulfate is dissolved, and barium chloride is added. The barium ions react with the sulfate ions to form solid barium sulfate. Neither the chloride nor the ammonium ions form a precipitate, so will stay in solution. The solid barium sulfate is extracted by filtration and weighed.

Simple stoichiometric calculations allow the calculation of the sulfate content of the barium sulfate solid. Then a percentage mass of sulfate is calculated using the following formula:

$$\%\ \text{mass sulfate} = \frac{\text{mass of sulfate in precipitate}}{\text{mass of fertiliser sample}} \times 100$$

So if a 10.0 gram sample of fertiliser contains 3.4 grams of sulfate ions, its percentage mass is:

$$\%\ \text{mass sulfate} = \frac{3.4}{10.0} \times 100 = 34\%$$

Volumetric methods

Volumetric analysis titrations are also useful in the analysis of fertiliser content. Many fertilisers contain nitrogen-based compounds that can be used in a back titration. Ammonium ions present in the fertiliser are boiled with sodium hydroxide to form ammonia and water:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$



To learn about volumetric analysis calculations and techniques, refer to Chemistry sections 4.3 and 4.4, pages 232 and 234.

An excess of hydroxide ions is used in this reaction. When the ammonium ions have all reacted, the excess hydroxide ions are titrated against a solution of hydrochloric acid. The amount of excess hydroxide ions allows for determination of the amount of hydroxide ions that reacted with the ammonium ions in the fertiliser. From this, a percentage mass or concentration of ammonium ions in the fertiliser sample can be determined.

Redox titrations are also used to determine the content of metal ions such as iron. Iron is used in fertilisers to prevent moss growth on plants and lawns. Titrating the iron(II) ions against potassium permanganate allows measurement of the iron(II) ion content of the fertiliser. The equation for this reaction is:

$$5Fe^{2+} + 8H^+ + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk. (ACSCH085 and ACSCH123) AC

Environmental issues – eutrophication

As fertilisers are washed off gardens and agricultural fields, they often make their way into lakes and rivers. Phosphates and nitrates are nutrients for algae that live in waterways. The enrichment of waterways by addition of these nutrients is called eutrophication. When excess nutrients from fertilisers are released into a waterway, algae can experience extremely fast growth rates. In extreme situations, the algae form thick layers on the surface of the water, as seen in Figure 2.32.

When thick algal blooms form, sunlight is prevented from entering the water. Plants that grow underwater cannot photosynthesise without sunlight, so they die. Reduction of photosynthesis from underwater plants results in a lack of oxygen in the water. A lack of oxygen in the water means animals will also die because they have no oxygen to breathe. As the animals and the algae die, they undergo anaerobic decay in the low oxygen environment. This results in the production of such toxic chemicals as methane, ammonia, hydrogen sulfide and phosphine. These poison the waterways so they are unsafe for drinking, recreation or as a water supply for agriculture.

Problems with eutrophication have become so severe, that in some places the use of fertilisers is regulated. In some parts of the United States, the waterways are so polluted that householders are banned from using fertilisers in their gardens to prevent run-off into the river systems. In Australia, the Murray River suffers from algal blooms, and farmers are sometimes asked to limit fertiliser use or prevent run-off into the river to decrease the amount of nutrients available to the algae.



sauletas/Shutterstock.com

◀ **Figure 2.32**
Algal blooms in a waterway

Making useful chemicals

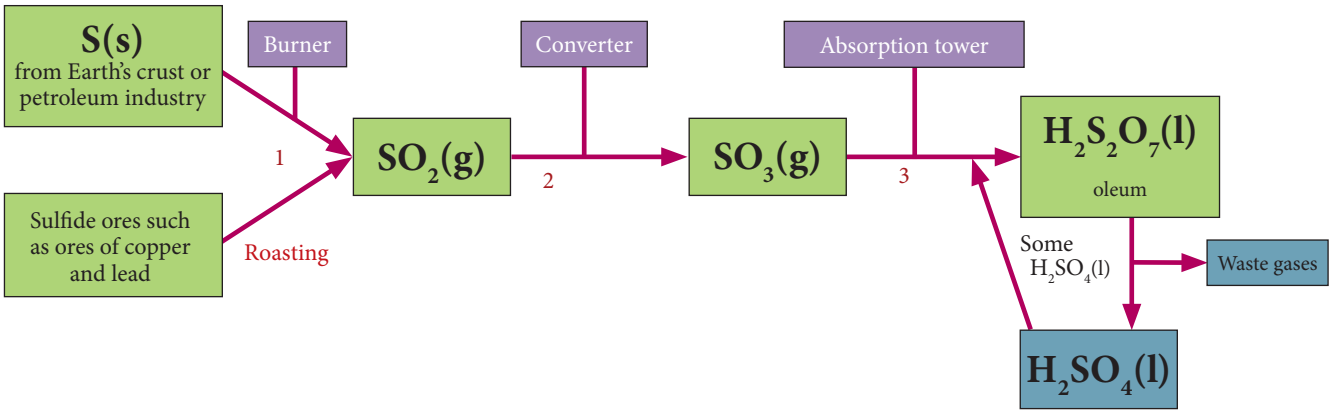
Many chemicals around the house or in the school laboratory are produced by industrial chemical processes. Chemicals that are produced on a large scale include acids such as sulfuric acid and nitric acid. Bases such as sodium hydroxide, lime and sodium carbonate are also produced in large volumes. Many of these chemicals are then used in other processes; for example, fertiliser and metal production. The chemical industry also makes products such as fuels and plastics and pure elements such as oxygen and nitrogen.

Production of sulfuric acid

One of the most important chemicals produced and used worldwide is sulfuric acid. Sulfuric acid is used in metal production, and in the production of paints, fertilisers, car batteries, detergents, dyes and fibres and in agriculture.

The process for making sulfuric acid is called the **contact process**. This allows high-concentration sulfuric acid to be produced in large quantities. The process has a number of stages, as seen in the flowchart in Figure 2.33.

▼ **Figure 2.33**
Stages of sulfuric acid production



In stage 1, sulfur is burnt in air to create sulfur dioxide:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

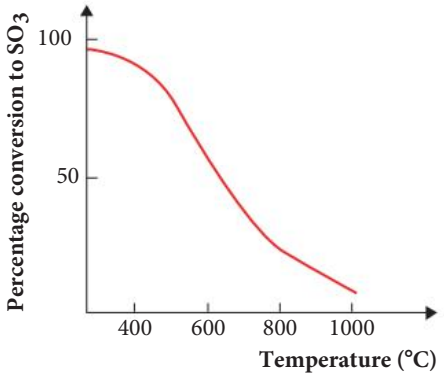
Sulfur dioxide can also be produced by burning metal sulfides such as zinc sulfide in air:

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

In stage 2, sulfur dioxide and air are reacted in the presence of a vanadium pentoxide catalyst (V_2O_5). This is done at a temperature of 450°C and at atmospheric pressure. The product, sulfur trioxide, forms as follows:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -99 \text{ kJ mol}^{-1}$$

▼Figure 2.34
Yield of sulfur trioxide as temperature changes



The key step in this process is the formation of sulfur trioxide. This is considered to be the limiting step in the entire process and is another example of an industrial compromise, similar to that seen in the Haber process. Normally, a way to increase the rate of a reaction is to increase the temperature. This gives the particles more energy and more productive collisions occur per unit time, and the rate of reaction increases.

However, if the equilibrium nature of the reaction is considered, a problem arises. The reaction has a negative enthalpy value, so if high temperatures are used to increase the rate of reaction, the reverse reaction will be favoured and the yield of products will decrease. This can be seen in Figure 2.34.

By using Le Chatelier's principle and looking at temperature and pressure, the following reaction conditions are predicted. A high pressure is favoured as there are fewer molecules on the product side. High pressure favours the side of fewer molecules as this will reduce the pressure and oppose the external change made. Thus, the yield of sulfur trioxide will increase. In reality, the pressure used is atmospheric pressure. Although a theoretical increase in yield would occur, the actual increase in yield would not justify the cost of increasing the pressure of the reaction.

A low temperature means the reaction will favour the exothermic direction as production of heat will oppose the external change made. This is where the problem lies. While a low temperature favours yield, it slows the rate of reaction so that the process becomes economically non-viable. The actual temperature used of 450°C for this step is a compromise between the yield and the reaction rate. In order to help the reaction rate, a vanadium pentoxide catalyst is used.

In stage 3, the sulfur trioxide that is formed is mixed with sulfuric acid to form a product called oleum ($H_2S_2O_7$). Oleum is the form in which sulfuric acid is stored and transported as it is less corrosive than a dilute sulfuric acid solution so less damage is done to tanks and transport vehicles.

When required, the oleum is diluted with water to form sulfuric acid:

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

Environmental issues – chemical spills

People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk. (ACSCH085 and ACSCH123)

The major environmental issue in the production, transport, use and storage of these chemicals is what happens in case of a spill. Spills can be caused by fires, explosions, leaks or damage to transport vehicles or storage tanks.

One of the worst chemical spills was the Bhopal disaster that occurred in India. In December 1984, a gas leak occurred at the Union Carbide India pesticide plant. Half a million people were exposed to methyl isocyanate and other gases. Methyl isocyanate is a toxic chemical that causes problems when inhaled or when skin contact occurs. People exposed can suffer chest pains and chemical burns. At high concentrations, it can cause pulmonary oedemas, haemorrhages and death.

An official death toll from this disaster has never been confirmed, but confirmed deaths number at least 3000, with reports of up to 8000 people dying as a result of chemical exposure. Tens of thousands of people suffered chemical burns, and other injuries.

The Bhopal disaster resulted in emergency plans being reviewed and, in many cases, implemented all over the world. In the United States, an Emergency Planning and Community Right-to-know Act was implemented that requires companies to provide information about the chemicals they are using, storing and transporting and to submit plans for spills, leaks and other emergencies. Today, these plans and laws are commonplace all over the world.

ACTIVITY 2.3

PRODUCTION OF OTHER CHEMICALS

Aim

To investigate the production of other useful chemicals

What to do

1. Individually, in pairs or small groups, research the production of a common chemical such as nitric acid, sodium carbonate or sodium hydroxide.
2. Create a flowchart of the process using the guidelines given earlier in the chapter. This should include:
   - identification of raw materials, waste products and any by-products
   - energy use and recycling in the process
   - equations of the chemical reactions at each stage
   - explanations of the relevant chemistry of each stage.
3. Compare your final flowcharts to those of other groups who investigated a different chemical process. Identify similarities and differences between the different production methods.

ACTIVITY 2.4

INVESTIGATING A MAJOR CHEMICAL SPILL

Aim

To investigate the causes and consequences of a major chemical spill

What to do

1. Individually, in pairs or small groups, research a major chemical spill.
2. Identify:
   - the chemicals that were leaked, spilled or caused other problems
   - the symptoms and consequences of human, animal or other environmental contact with these chemicals
   - the causes of the leak, spill or disaster
   - laws or regulations that were put into place as a result of this event (if applicable).

CHAPTER SUMMARY

- Production of chemicals involves different chemical and physical processes that change the chemical composition or physical state of a chemical. Energy use must be planned for, including the recycling of energy and the use of alternative energy sources where possible. Flowcharts can be used to represent the production of a chemical and can be analysed to describe the production process.
- Zinc metal production involves concentration of the mineral by froth flotation, then conversion by chemical processes to a form suitable for electrolytic reduction. Reduction from zinc ions to zinc metal is done by aqueous electrolysis. The zinc metal produced is sufficiently pure for use in galvanising to prevent corrosion of metals such as steel.
- The refining of iron, aluminium and copper has some similarities to zinc refining but also has many differences. Reduction to iron metal occurs through chemical reduction with carbon in a blast furnace rather than electrolysis. Aluminium electrolysis must occur with a molten salt due to the high activity of aluminium, but is not necessary for zinc electrolysis. Copper refining is performed by electrolysis to further purify copper for electrical conductivity uses.
- Intensive energy use in metal production leads to production of large amounts of carbon dioxide, which contributes to the enhanced greenhouse effect. Production of sulfur dioxide results from the removal of sulfur from metal sulfide ores. Sulfur dioxide contributes to the formation of acid rain, but can be addressed by collection of the sulfur dioxide formed and conversion into sulfuric acid.
- The Haber process is the production of ammonia, the first step in the production of nitrogen-based fertilisers. The efficient production of ammonia is a balance between a fast rate of reaction and an appropriate yield. Analysis of fertilisers occurs through gravimetric and volumetric analysis.
- The phosphates and nitrates in fertilisers can contribute to eutrophication of waterways. The nutrients encourage algal growth, which can have many negative effects on a waterway and prevent its use as a water supply or for recreation.
- The production of sulfuric acid involves the multistep contact process, including the key step of formation of sulfur trioxide. This is an example of an industrial compromise between rate of reaction and yield of product.

CHAPTER GLOSSARY

acid rain rain of low pH; results when chemicals such as sulfur and nitrogen oxides are released, leading to the production of acids in the atmosphere

by-product a product resulting from a chemical process that is not the desired end product, but still has commercial value

contact process the industrial process for producing sulfuric acid

enhanced greenhouse effect the trapping of excess heat in the Earth's atmosphere due to increased production of greenhouse gases such as carbon dioxide through human activity

froth flotation a method for concentrating a metal ore through use of collectors and frothing agents; developed in Australia

Haber process the industrial process that combines nitrogen and hydrogen gases to produce ammonia on a large scale

mineral a compound with a fixed chemical composition

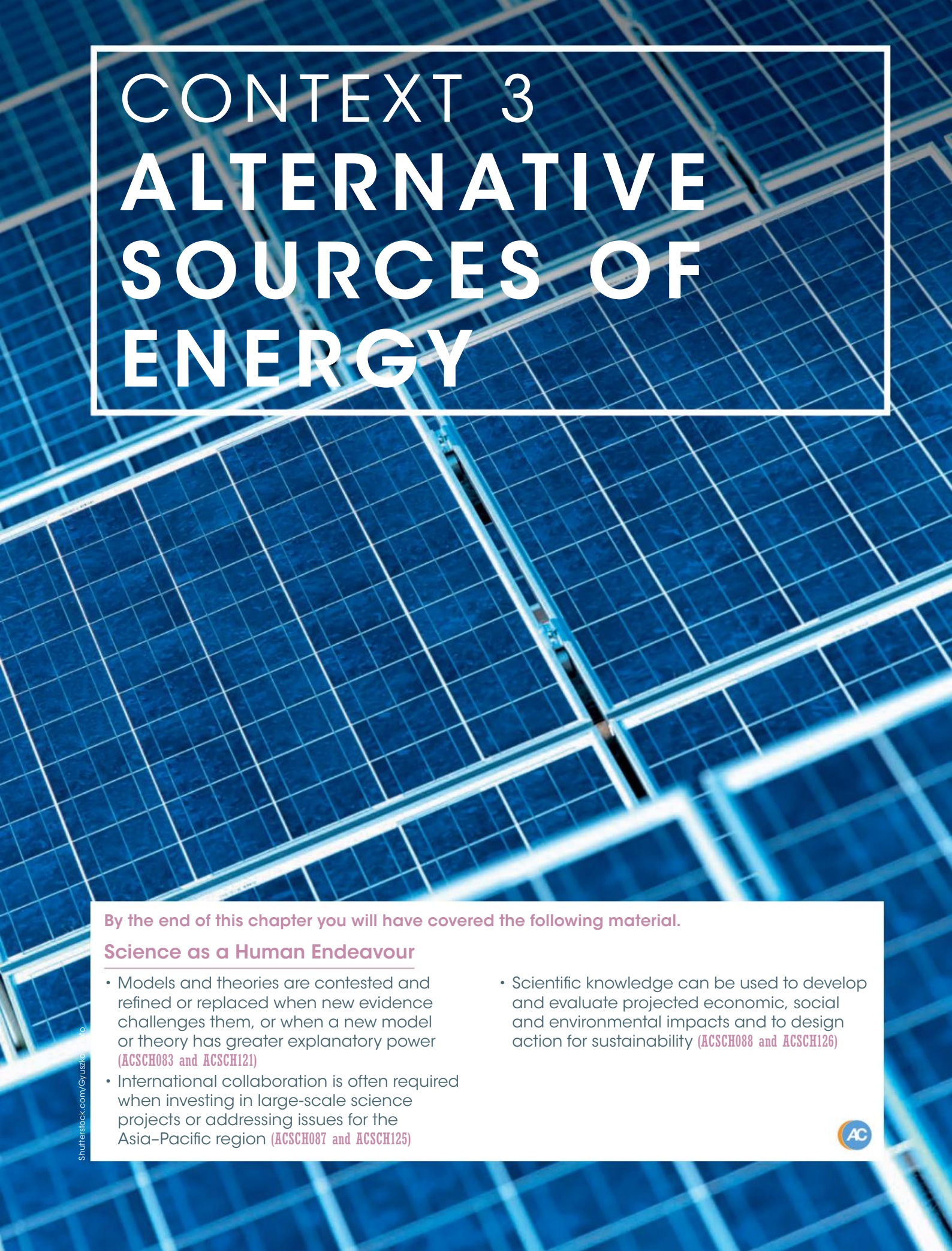
ore a mixture of chemicals that contains one in sufficient quantity to be economically viable to extract

raw material a material used in a chemical process that is readily available but not highly processed, including air, coal and sand

waste product product from a chemical process that has no commercial value or is toxic or dangerous

yield the amount or percentage of the possible product that is actually produced

CONTEXT 3
ALTERNATIVE SOURCES OF ENERGY



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By the end of this chapter you will have covered the following material.

Science as a Human Endeavour

- Models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory power (ACSCH083 and ACSCH121)
- International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region (ACSCH087 and ACSCH125)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCH088 and ACSCH126)

Contextual story – Alternative sources of energy

- Redox chemistry – the first steps
- Examples of batteries
- Examples of rechargeable batteries
- Solar cells relating properties to uses
- Fuel cells – variety and their uses
- Microbial fuel cells – latest advances
- Developing sustainable solutions for generating electricity

Science as a Human Endeavour (SHE)

- Models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory power (ACSCH083 and ACSCH121)
- International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region (ACSCH087 and ACSCH125)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCH088 and ACSCH126)

Chemical understanding

- What are redox reactions?
- Reactivity and the periodic table
- Oxidation states
- Types of redox reactions – corrosion, combustion and displacement reactions of metals
- Standard electrode potentials (SEP)
- Galvanic cells
- Using SEP to determine cell potentials
- Fuel cells
- Electrolytic cells

Science Understanding (SU)

- A range of reactions, including displacement reactions of metals, combustion, corrosion, and electrochemical processes, can be modelled as redox reactions involving oxidation of one substance and reduction of another substance (ACSCH103)
- Oxidation can be modelled as the loss of electrons from a chemical species, and reduction can be modelled as the gain of electrons by a chemical species; these processes can be represented using half-equations (ACSCH104)
- The ability of an atom to gain or lose electrons can be explained with reference to valence electrons, consideration of energy, and the overall stability of the atom, and can be predicted from the atom's position in the periodic table (ACSCH105)
- The relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials (ACSCH106)
- Electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction half-reactions connected via an external circuit that allows electrons to move from the anode (oxidation reaction) to the cathode (reduction reaction) (ACSCH107)
- Galvanic cells, including fuel cells, generate an electrical potential difference from a spontaneous redox reaction; they can be represented as cell diagrams including anode and cathode half-equations (ACSCH108)
- Fuel cells can use metal nanoparticles as catalysts to improve the efficiency of energy production (ACSCH109)
- Cell potentials at standard conditions can be calculated from standard electrode potentials; these values can be used to compare cells constructed from different materials (ACSCH110)
- Electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur, and can be used in small-scale and industrial situations (ACSCH111)

Investigations

Chemistry 5

- Investigation 5.1 Factors that affect electrolysis
- Investigation 5.2 Factors that affect the rate of an electrolysis reaction

Science Inquiry Skills (SIS)

- Identify, research, construct and refine questions for investigation; propose hypotheses; and predict possible outcomes (ACSCH074)
- Design investigations, including the procedure/s to be followed, the materials required, and the type and amount of primary and/or secondary data to be collected; conduct risk assessments; and consider research ethics (ACSCH075)
- Conduct investigations, including using volumetric analysis techniques and constructing electrochemical cells, safely, competently and methodically for the collection of valid and reliable data (ACSCH076)
- Represent data in meaningful and useful ways, including using appropriate graphic representations and correct units and symbols; organise and process data to identify trends, patterns and relationships; identify and distinguish between random and systematic errors, and estimate their effect on measured results; discuss how the nature of the procedure and the sample size may influence uncertainty and limitations in data; and select, synthesise and use evidence to make and justify conclusions (ACSCH077)
- Interpret a range of scientific texts, and evaluate processes, claims and conclusions by considering the quality of available evidence, including confidence intervals in secondary data; and use reasoning to construct scientific arguments (ACSCH078)
- Select, construct and use appropriate representations, including half-equations, balanced chemical equations, equilibrium constants and expressions, pH, oxidation numbers, standard electrode potentials and cell diagrams, to communicate conceptual understanding, solve problems and make predictions (ACSCH079)
- Select and use appropriate mathematical representations to solve problems and make predictions, including calculating cell potentials under standard conditions, using the mole concept to calculate moles, mass, volume and concentrations from volumetric analysis data, determining the yield of incomplete reactions, and calculating the pH of solutions of strong acids and bases (ACSCH080)
- Communicate to specific audiences and for specific purposes using appropriate language, nomenclature, genres and modes, including scientific reports (ACSCH081)

Introduction

Fossil fuels have been used for several hundred years as a source of energy. Their discovery led to the beginning of the Industrial Revolution in the late 18th century. Kerosene was used for streetlights. Coal was used in furnaces. Industry moved from small-scale operations where people worked using small hand tools in their backyards to large factories where much larger-scale operations occurred. The steam engine was invented – it was used to power locomotives, boats and factories. Coal was the fuel for many of these steam engines. Eventually, as industrialisation increased and technology improved, other fossil fuels were also utilised. Coal was still used for power stations; however, various fractions of petroleum were used in cars, trucks, buses and aeroplanes.



Science Museum/Science & Society Picture Library

▲ **Figure 3.1**
Furnace used during the Industrial Revolution

The use of fossil fuels is a well-known example of the transformation of chemical energy to another form of energy, namely heat energy, through the chemical process of combustion. The heat energy, in turn, is transformed to other forms of energy, such as mechanical energy and electrical energy. A less well-known example of a transformation of chemical energy to another form of energy is oxidation–reduction chemistry, commonly referred to as redox chemistry. In this case, chemical energy is transformed directly to electrical energy. This also occurred during the Industrial Revolution.

Oxidation–reduction chemistry resulted in the development of the battery. Batteries allowed devices to become portable – they did not need to be plugged into mains power as they contained their own electrical energy supply. As understanding of oxidation–reduction chemistry increased, a range of batteries was developed. Different batteries used different



Gleb Semenov/Dreamstime.com



CLIPAREA / Custom media/ Shutterstock.com



Hugh Threlfall/Alamy



Dreamzmaniac/Dreamstime.com

◀ **Figure 3.2**
Some examples of 'plugged in' and portable devices: desktop computer and tablet, sound system and iPod

chemicals for the redox reactions. This enabled batteries to be developed that had different voltages, which in turn had different uses. Batteries have also been miniaturised, which has led to the development of smaller, more portable devices. Batteries are now used in many devices, including computers, mobile sound systems, hearing aids and heart pacemakers.

The discovery of a number of elements in the early 1800s, including aluminium, barium, magnesium and sodium, was the result of using processes involving oxidation–reduction chemistry. These elements are very reactive and could not be isolated from the compounds in which they naturally occured until English chemist and inventor Sir Humphry Davy (1778–1829) developed the process of electrolysis. Electrolysis is still used extensively in industry for extracting metals from their ores and purifying metals.

This chapter will trace the development of our understanding of oxidation–reduction chemistry and its application as an important source of energy that has changed how we live. It will also look at current developments in redox chemistry, especially the development of fuel cells, and their potential impact on both society and the environment. Fossil fuels are a finite resource. Fuel cells have the potential to be used in cars, replacing petroleum products.

We cannot take all of the technologies in the world for granted. We need to understand the chemistry and invest in science if we are to maintain and further develop products that society needs. We also need to be responsible custodians of our planet so that future generations can also enjoy it. Fuel cells have the potential to provide energy without the emission of harmful pollutants. However, there are still areas that need to be addressed, especially in the materials used as catalysts, to enable fuel cells to be efficient enough so that they are economically viable to use.

Redox chemistry – the first steps

Models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory power. (ACSCH083 and ACSCH121) AC

Oxidation–reduction chemistry is now a major area of chemistry. However, it was not always the case. As with anything, there had to be a beginning – a starting point from which other scientists further developed our understanding. That starting point is generally acknowledged as being the work of Italian anatomist and physician Luigi Galvani (1737–98) in the 1780s.

Galvani and Volta

Luigi Galvani was born in Bologna, Italy. He was educated at the University of Bologna and later took up a position as a lecturer and professor at that institution. Galvani conducted a great deal of research on the electrical signals in the nervous systems of frogs.

In 1791, Galvani published a book on his experiments and findings about the effect of electricity on muscular motion. The book, *De Viribus Electricitatis,* has five main parts:

- Part One – The effects of artificial electricity on muscular motion
- Part Two – The effects of atmospheric electricity on muscular motion
- Part Three – The effects of animal electricity on muscular motion
- Part Four – Conjectures and some conclusions
- Two letters between Doctor Luigi Galvani and Don Bassano Carminati, Public Professor of Medicine in the University of Pavia.

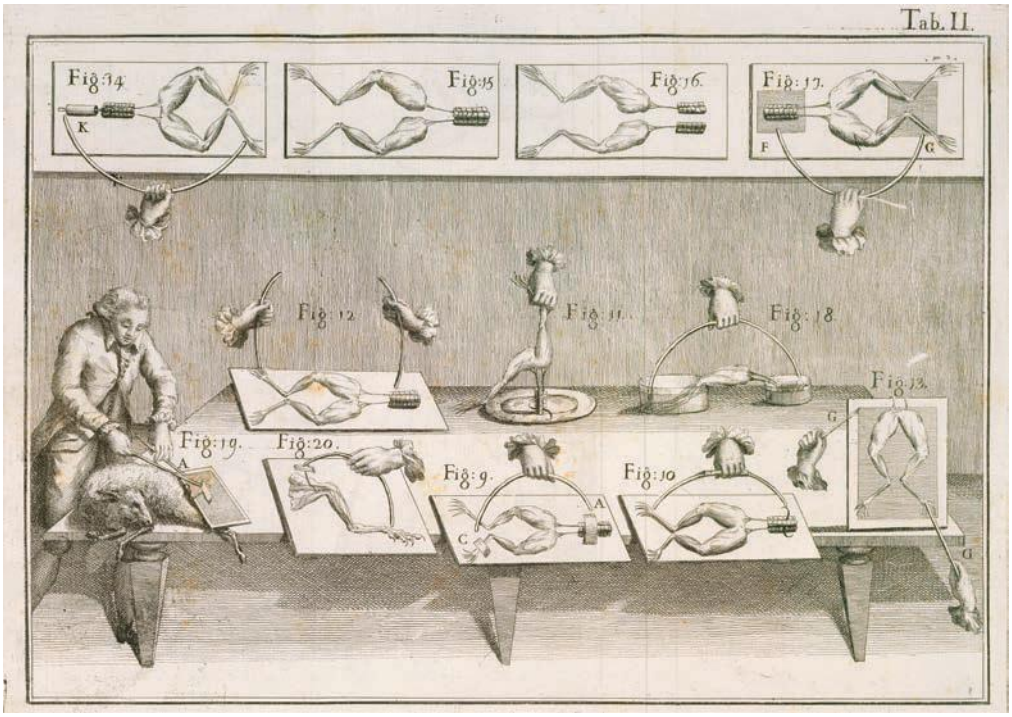
Galvani conducted many experiments on frogs by connecting the frog to a Leyden jar – a jar that could store electricity, which was invented in the 1740s. In all cases, the dead frog 'jumped vigorously about'.

Part Three of Galvani's book was to be the beginning of electrochemistry, although Galvani was not aware of it at the time. There are many stories about Galvani's work, each of them including slightly different information about either the metals used or the position of the frog. Hence, it is important that we accurately report Galvani's work. Let's allow Galvani to tell his own story. In *De Viribus Electricitatis* (1791), Galvani wrote (page 40):
'I had sometimes seen prepared frogs placed in iron gratings which surrounded a certain hanging garden of my house, equipped also with bronze hooks in their spinal cord, fall into the customary contractions, not only when the sky was lighting, but also sometimes when it

was quiet and serene, I thought these contractions derived their origin from the changes which sometimes occur in atmospheric electricity'.

To remove any effects due to atmospheric electricity, Galvani conducted further experiments. Galvani wrote (page 41): 'But when I had transported the animal into a closed chamber and placed him on an iron surface, and had begun to press against it the hook fixed in his spinal cord, behold the same contractions and the same motions! Likewise continuously, I tried using other metals, in other places, other hours and days; and the same result; except that the contractions were different in accordance with the diversity of metals, namely more violent in some, and more sluggish in others. Then it continually occurred to me to employ for the same experiment other bodies, but those which transmit little or no electricity, glass for example, gum, resin, stone, wood, and those which are dry; nothing similar occurred, it was not possible to observe any muscular motions or contractions. Results of this sort both brought us no slight amazement and began to arouse some suspicion about inherent animal electricity itself. Moreover both were increased by the circuit of very thin nervous fluid which by chance we observed to be produced from the nerves to the muscles …'

Galvani found that while there was a metal in contact with the frog's spinal cord and another in contact with its muscle and there was a complete circuit, the frog's legs contracted regardless of whether another source of electricity (lightning or the Leyden jar) was present or not. He concluded that the electricity was emanating from the frog itself; hence, the term 'animal electricity'.



Electrical experiments/British Library, London, UK/© British Library Board. All Rights Reserved/The Bridgeman Art Library

◀ **Figure 3.3**
Diagram of Galvani's experiments on frogs

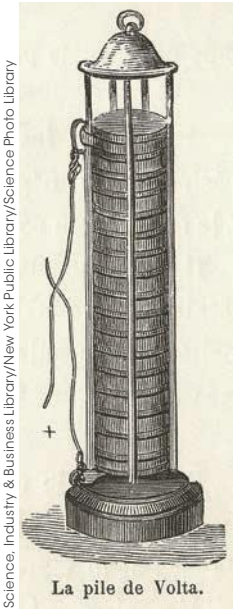
Alessandro Volta was a contemporary of Luigi Galvani. He was born in Como, Italy, in 1745. In 1779, Volta was appointed the Professor of Physics at the University of Pavia. While there, he invented the voltaic pile, the first device that could produce a constant supply of electricity.

Galvani sent a copy of his work to Volta. Volta did not agree with the conclusions that Galvani drew from his work. Volta thought that the contraction of the frog's muscle was an effect of the electricity, not the source of the electricity. He thought that it was the contact of the different metals that produced the electricity. Volta set out to prove Galvani wrong. Volta's disagreement with Galvani split the Italian scientific community. This controversy raged for nearly 10 years, certainly for the remainder of Galvani's life. Galvani died in 1798.

Volta experimented with different metals; however, the instrumentation available at the time was not sensitive enough to measure the small currents, so Volta used his tongue as the detector. The saliva in his mouth acted as an electrolyte, like the frog's tissue in Galvani's experiments. However, this was not conclusive evidence that 'animals' were not needed to produce electricity.

DE VIRIBUS ELECTRICITATIS

Read this translation of Galvani's publication on the effect of electricity on muscular motion – Galvani's work in his own words. He describes the experiments that he undertook and the conclusions that he drew from those experiments.



Science, Industry & Business Library/New York Public Library/Science Photo Library

Figure 3.4 ▲ Volta's voltaic pile was the first device that could produce a constant supply of electricity.

Volta then soaked pasteboard in **brine**, a saltwater solution, and placed it between alternating discs of two different metals. He placed a silver disc on the bottom, a zinc disc on top of it, then a piece of the moistened pasteboard. He continued with this arrangement until it was as high as possible without falling over. When Volta connected them, he showed that a current flowed.

Volta used different combinations of metals and found alternating discs of silver and zinc produced the greatest current. Adding more discs produced more current. If he used about 20 couples of these metal discs, the current could be measured using an electrometer designed by Italian physicist Tiberius Cavallo (1749–1809). Hence, he was able to show that no animals were needed to produce electricity. This work was completed in 1800, 2 years after the death of Galvani.

The advantage of Volta's pile was that it provided a constant flow of electricity compared to the Leyden jar, which discharged suddenly. Volta had constructed the first battery. He had transformed chemical energy into electrical energy and utilised this flow of electricity. Although he had proved that Galvani's conclusions were incorrect, Volta's explanation of what caused the flow of electricity was also incorrect. He said that it was the contact of the metals that caused the electricity. He did not fully explain the role of the moistened pasteboard as the electrolyte. He did not realise that there was a chemical reaction occurring.

This is one of many examples through history of how ideas have changed as more evidence becomes available. The evidence is weighed up against the existing explanation. If there is sufficient evidence to refute the existing explanation, then scientists try to develop new explanations or modify existing ones to fit the growing body of knowledge about a particular concept. In this case, Volta's evidence did not support Galvani's explanation, so a new explanation was developed. Although this was also incorrect, it progressed understanding of using different metals to produce electricity. Other scientists further developed this work to more correctly explain the chemistry of the voltaic pile.

ACTIVITY 3.1

GALVANI AND VOLTA

Aim

To demonstrate a knowledge of Galvani and Volta's contribution to our understanding of electrochemistry

What to do

1. In pairs, develop a script for a discussion between Galvani and Volta on the relative merits of their work.
2. One person takes the role of Galvani while the other takes the role of Volta.
3. Create a short video of the discussion between Galvani and Volta.

ACTIVITY 3.2

VOLTAIC PILE

Aim

To explain the chemistry of the voltaic pile

What to do

Use your knowledge of the activity of metals and electrochemistry, and other sources if required, to write the reaction occurring at each of the metals in the voltaic pile consisting of silver and zinc and a saltwater electrolyte.

For more discussion on reactivity and oxidation and reduction equations, refer to Chemistry section 3.2, page 207.

Davy and Faraday

Sir Humphry Davy heard of Volta's pile and wanted to investigate its use. He used the voltaic pile to electrolyse potash (potassium hydroxide) and soda (sodium hydroxide), to isolate potassium and sodium.

Davy also isolated magnesium, calcium, strontium and barium; however, this was more of a challenge because he had to use a mercury cathode. Hence, he produced a mixture of the metal and mercury. Davy then isolated the metal by distilling off the mercury. Davy had successfully performed electrolysis experiments. Although he did not use this method to reverse the reactions of batteries in operation at the time, he was one of the earliest to utilise the voltaic pile to transform electrical energy to chemical energy.

Although Sir Humphry Davy was a brilliant chemist, some suggest that his greatest discovery was the scientist Michael Faraday (1791–1867). Faraday worked for Davy for several years in the early 1800s. However, he conducted many of his own experiments, initially in chemistry but eventually more in the physical sciences involving electricity. Faraday made two significant contributions to electrochemistry:

- the introduction of electrochemical terms such as 'electrode', 'electrolyte', 'anode' and 'cathode'
- two laws that are now known as Faraday's laws of electrolysis.

Faraday was the first to propose a quantitative relationship between the amount of current passing through a substance and the amount of substance that is decomposed. He used experiments on the decomposition of water to support his law. Others have built on Faraday's work to quantitatively understand electrolysis reactions, which is very important when looking at the economic viability of electrolytic processes. For example:

- What current needs to be applied to recharge a battery?
- How long will it take to recharge a battery?
- How much will it cost to recharge a battery?

HUMPHRY DAVY'S ARTICLE (1808)

Read Humphry Davy's description of the experiments he undertook to decompose compounds to isolate the alkali metals. This is Davy's work in his own words.

ON ELECTRICAL DECOMPOSITION (1834)

Read Faraday's description of his laws of electrolysis in which he introduces the new terms 'electrode', 'electrolyte', 'anode' and 'cathode'. This is Faraday's work in his own words.

WOW

Michael Faraday

England's class-based system was very evident during Faraday's early life. He was born into a working class family and was not considered a gentleman. Faraday journeyed through Europe with Sir Humphry Davy and his wife, Lady Davy, as Davy's scientific assistant and valet. Lady Davy made Faraday travel outside the coach and eat with the servants – he was not treated as an equal. Later in life, Faraday was a well-respected scientist in his own right. He was a very modest man who refused to accept a knighthood and twice turned down the opportunity to become President of the Royal Society.

ACTIVITY 3.3

TIMELINE OF SIGNIFICANT HISTORICAL EVENTS IN ELECTROCHEMISTRY

Aim

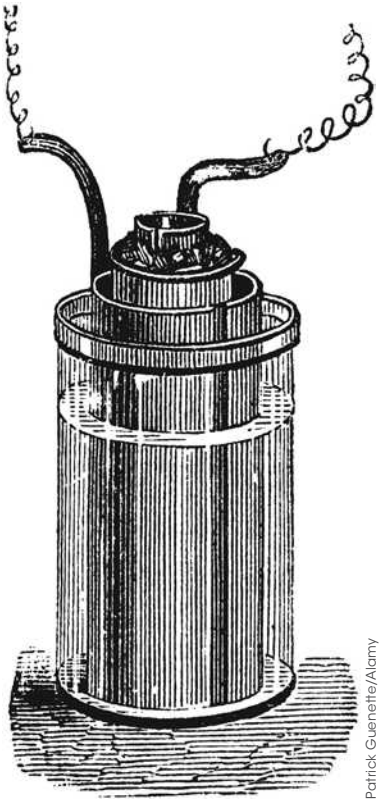
To develop a timeline of significant historical events in electrochemistry

What to do

1 Identify the significant contributions of Galvani, Volta, Davy and Faraday to our understanding of electrochemistry.

2 Draw a timeline of these contributions. Your timeline may be presented:
   - by hand
   - using a spreadsheet program such as Microsoft Excel or Apple Numbers
   - using a web-based application such as Timetoast.

For more discussion on galvanic cells, refer to Chemistry section 5.3, page 257.



Patrick Guenette/Alamy

Figure 3.5 ▶ The original Daniell cell

Batteries

Galvani and Volta both made a significant contribution to the beginning of the story about the development of portable sources of electricity. However, while the voltaic pile was a useable battery, there were issues that needed to be addressed if it was to be used on a larger scale. One of these issues was how to produce a constant voltage over an extended period of time. To address this issue, scientists needed to overcome the problem of hydrogen forming in the cell. The English chemist and meteorologist John Frederic Daniell (1790–1845) developed the first commercial galvanic cell.

Daniell cell

The original Daniell cell, developed by John Frederic Daniell in 1836, consisted of a piece of copper placed in the bottom of a glass jar covered in a copper(II) sulfate solution. A piece of zinc was then suspended in the jar and a zinc sulfate solution was gently poured into the jar. Since zinc sulfate is less dense than copper(II) sulfate, on careful pouring, the zinc sulfate will 'float' on top of the copper(II) sulfate solution.

The Daniell cell was then modified so that both electrodes were accessible by placing the solutions beside each other with a separator in between. However, each metal was still in contact with its own solution. This made it easier to connect the electrodes to the external circuit.

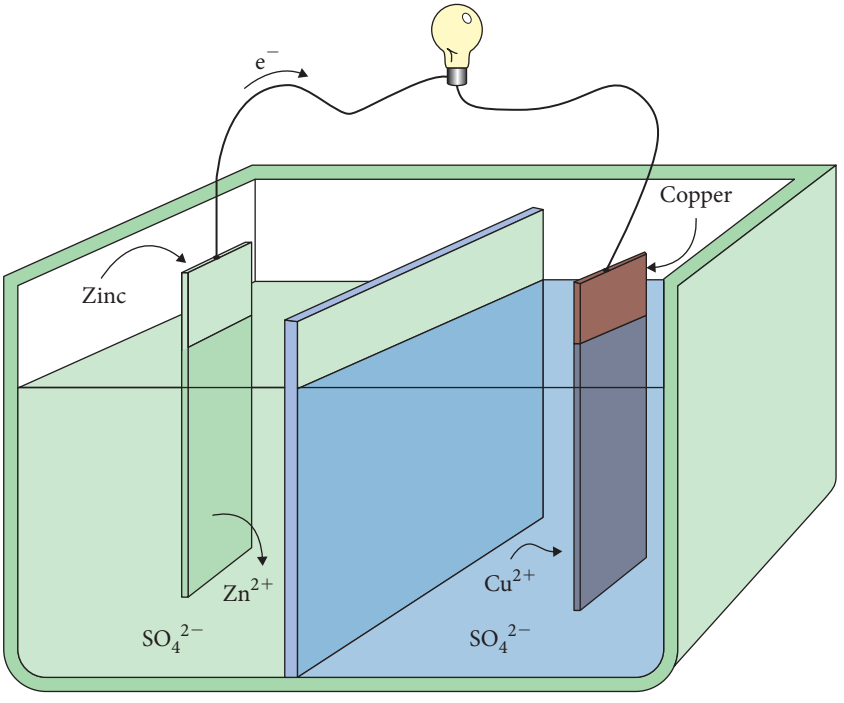
WOW

Patenting a salt bridge

George A. Perley applied for a patent for the 'salt-bridge tube and method of producing it' on 1 April 1942. The patent was granted on 28 March 1944. Its patent number is US2345498.

DANIELL CELL

View this simple animation, which shows what is happening at the anode and cathode of the Daniell cell.



Adapted from Roberge, P. R. (2008) *Corrosion Engineering: Principles and Practice*, McGraw-Hill Education

▲ **Figure 3.6** Modified Daniell cell

The Daniell cell half-reactions are:

- Anode $Zn(s) \rightarrow Zn^{2+} + 2e^-$
- Cathode $Cu^{2+} + 2e^- \rightarrow Cu(s)$

Zinc is more reactive than copper, so it was oxidised while the copper was reduced.

This was the first galvanic cell that was both practical and reliable. It was used to power the telegraph – the first method for transmitting messages electronically over large distances. However, the Daniell cell was fragile and fairly large, and it was not sealed. Therefore, it was limited in terms of its applications.

Reactivity is discussed in Chemistry section 3.2, page 207.

ACTIVITY 3.4

IMPACT OF THE TELEGRAPH

Aim

To research methods of communication prior to the use of the telegraph

What to do

Use several sources to research methods of communication over short and long distances prior to the introduction of the telegraph.

What did you discover?

How did the introduction of the telegraph affect society?

Leclanché cell

To revise oxidation states, refer to Chemistry section 3.5, page 218.

The Leclanché cell was developed and patented by French engineer Georges Leclanché (1839–82) in 1866. The original Leclanché cell contained solutions, so it was called a wet cell. The cathode of the Leclanché cell consisted of graphite powder and solid manganese(IV) dioxide (MnO_2) with a carbon rod in it. This was packed into a porous pot. The porous pot was placed into an ammonium chloride solution along with a zinc rod, which was the anode. The ammonium chloride was the electrolyte that seeped through the porous pot to make contact with the cathode.

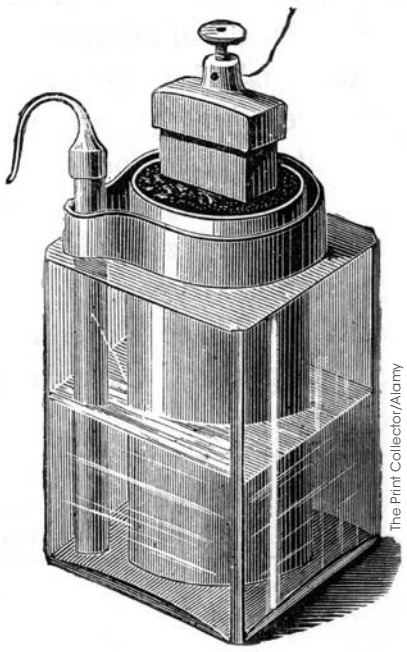
The Leclanché cell half-reactions are:

- Anode $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
- Cathode $2MnO_2(s) + 2NH_4^+ + 2e^- \rightarrow 2MnO(OH)(s) + 2NH_3(aq)$

The zinc is oxidised to form zinc ions while the manganese is reduced from manganese(IV) to manganese(III).

Within two years of Georges Leclanché patenting his cell, more than 20 000 of his cells were being used for the telegraph system. It was also used to power early telephones, since each telephone needed its own electricity source. However, as telephone conversations became longer and the calls were made over longer distances, limitations were identified, namely that the battery ran down and the conversation was inaudible by the end of the call.

Over time, modifications to the Leclanché cell improved its performance. Between 1920 and 1980, there was over a 700% improvement. One improvement was replacing the ammonium chloride solution with an ammonium chloride paste.



▲ **Figure 3.7**
The original Leclanché cell

The modern Leclanché cell consists of a carbon rod as the cathode, in the centre of the cell. It is surrounded by solid manganese(IV) dioxide and graphite powder, which in turn is surrounded by a mixture of ammonium chloride and zinc chloride paste. A zinc anode encases the entire cell. However, a limitation of this cell is that the slightly acidic ammonium chloride corrodes the zinc casing, which causes the battery to leak. Since the ammonium chloride solution has been replaced with a paste, this cell is commonly referred to as a dry cell.

The dry cell battery is used today in clocks, stopwatches and electric starters for barbecues. Dry cell batteries were more widely used 10–20 years ago in electronic goods, such as cameras, radios and portable sound systems. Since then, the zinc–carbon dry cell battery has been replaced in many appliances with either alkaline batteries or other types of batteries. The alkaline battery is very similar in construction to the zinc–carbon dry cell, but it has a potassium hydroxide electrolyte rather than ammonium chloride. Hence, the electrolyte is a basic salt rather than an acidic salt.



Figure 3.8 ▶
Dry cell batteries

ENERGISER – HOW BATTERIES WORK

View the simple animations and read the descriptions of an alkaline battery to see battery parts, how to construct a battery and how it is powered.

The chemistry for the alkaline battery is:

- Anode: $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$
- Cathode: $2MnO_2 + 2H_2O + 2e^- \rightarrow 2MnO(OH) + 2OH^-$

The anode reaction still consists of the oxidation of zinc from elemental zinc to zinc ions while the cathode reaction still involves the reduction of manganese(IV) to manganese(III). The alkaline battery can deliver a higher current and a more consistent voltage over longer periods of time than the traditional dry cell battery. Hence, it has largely replaced the dry cell battery for uses such as flash units for cameras.

Lithium batteries

Lithium batteries are not to be confused with lithium–ion batteries. Lithium batteries are non-rechargeable batteries. They are much smaller than normal dry cell batteries; hence, they have enabled the development of smaller devices. The CR 2032 is a common lithium battery. It is about the size of a 10-cent coin; therefore, it is sometimes referred to as the coin cell battery. It is commonly used in watches, bathroom scales, blood glucose testing meters and electric thermometers. It has a voltage of about 3 V and has a long life due to its large charge density.

To learn how to determine cell potential, refer to Chemistry section 5.4, page 258.

Lithium is more easily oxidised than zinc. The half equations for the oxidation of lithium and zinc are:

$$Li(s) \rightarrow Li^+ + e^- \qquad E° = +3.04\,V$$
$$Zn(s) \rightarrow Zn^{2+} + 2e^- \qquad E° = +0.76\,V$$

The table of standard electrode potentials is in Chemistry Table C5.1, page 256.

So, if a lithium anode is used instead of a zinc anode, then the cell voltage will be much larger. The voltage of common lithium batteries is comparable to two alkaline batteries, but physically a lithium battery is much smaller. The lithium battery always consists of a lithium anode; however, the cathode and electrolyte can change. A common lithium battery uses a manganese(IV) dioxide cathode.

ACTIVITY 3.5

SILVER OXIDE CELL

Aim

To research the silver oxide cell and justify its use

What to do

Research the silver oxide battery, including the:

- reaction at the anode
- reaction at the cathode
- electrolyte used
- advantages and disadvantages or limitations of its use.

Rechargeable batteries



For more information on electrolytic cells, which are the basis for recharging batteries, refer to Chemistry section 5.6, page 266.

Batteries have been used for more than 150 years. Primary batteries were unable to be recharged. They were used and then thrown away. However, there are other batteries that can be recharged – these are called secondary batteries.

Secondary batteries have two different phases, the:

- discharge phase where they operate as normal batteries
- recharge phase where the reactions are reversed by applying an external electric current.

During the discharge phase, secondary batteries are galvanic cells. However, during the recharge phase, they are electrolytic cells. Rechargeable batteries are only possible when the original oxidation and reduction reactions can be reversed without other products also forming. Hence, it is only possible to recharge some batteries.

Lead–acid battery

The first battery that could eventually be recharged was developed by the French physicist Gaston Planté (1834–89) in 1859. He invented the lead–acid battery, which consisted of two sheets of lead separated by a linen cloth immersed in a bottle of sulfuric acid. Further refinement of his design included the use of a lead anode and a lead dioxide cathode separated by a strip of rubber. In 1860, he demonstrated nine cells connected together in series to the French Academy of Sciences. The common lead–acid battery used for starting engines in fossil-fuelled cars is generally six cells.

The major improvements of the lead–acid battery over the Daniell cell battery, which was also used at the time, were that it generated a much larger voltage of about 2 V instead of 1.1 V. It also only required a single electrolyte and, importantly, the reactions could be reversed when it was connected to another source of electric current. However, this was not possible until electrical power was readily available towards the end of the 19th century.

WOW

Gaston Planté

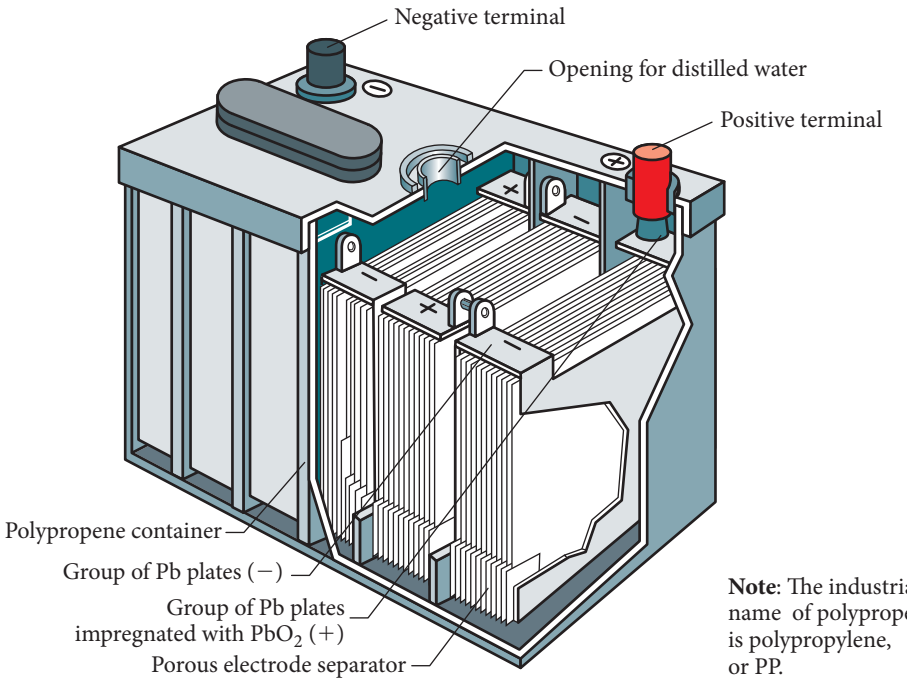
In 1855, at the age of 21, Gaston Planté was working for Henri Becquerel's father when he discovered the first fossils of the large flightless bird *Gastornis parisiensis*, which was named after him. This bird lived in the Paleocene, about 60 million years ago. It was about 1.75 metres high with large, powerful legs. It also had a large beak with a slightly hooked top. Scientists inferred that it was carnivorous. Scientists have not been able to determine its body covering but many of the pictures show it with a hair-like covering.



Jaime Chirinos/Science Photo Library

▶ **Figure 3.9**
Gastornis parisiensis

Figure 3.10 ▶
A lead–acid battery



Note: The industrial name of polypropene is polypropylene, or PP.

HOW A LEAD–ACID BATTERY WORKS

Watch this video, which explains the principles of a lead–acid battery in a motorbike.

LEAD–ACID BATTERY

Watch this video, which demonstrates how car batteries work.

The lead–acid cell consists of an anode and a cathode since it has oxidation and reduction reactions. However, it is more usual to describe the terminals in terms of their polarity, namely as positive and negative, because these terms are consistent throughout both the discharging and recharging phases.

The structure of a lead–acid battery is shown in Figure 3.10. The battery consists of lead plates, sulfuric acid as the electrolyte and lead plates coated with lead(IV) oxide (PbO_2). The reactions occurring at each of the terminals during discharge, when the battery is being used to start the engine or used to power the radio when the engine is not running, are:

- Negative terminal $Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$
- Positive terminal $PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

During discharge, at the negative terminal, the lead is oxidised from 0 to +2, while at the positive terminal, the lead is reduced from +4 to +2.

These reactions can be easily reversed by connecting the battery to an external power supply. In a car, the alternator is used to recharge the battery while the car is running. The alternator converts mechanical energy from the vehicle's pistons and crankshaft into electrical energy, which is then supplied to the battery and also used to operate the vehicle's accessories, such as the sound system, lights and horn. Although the reactions are reversible, this process is not 100% efficient – very small quantities of the products are not re-used in the recharge process. Hence, over time, there is less and less chemicals used for recharging and eventually all rechargeable batteries will need to be replaced.

During the recharge phase of the battery's operation, the following reactions occur.

- Negative terminal $PbSO_4(s) + H^+(aq) + 2e^- \rightarrow Pb(s) + HSO_4^-(aq)$
- Positive terminal $PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^-$

During the recharge phase, at the negative terminal, the lead is reduced from +2 to 0, while at the positive terminal, the lead is oxidised from +2 to +4. These reactions continue to occur while the battery is operating normally. However, as batteries get used over time, the charging and discharging process, combined with physical knocking, causes the battery plate material to be dislodged and lost. Deposited Pb can also form short circuits across battery cells.

WOW

Lead–acid batteries

In 1999, lead–acid batteries comprised almost half of all rechargeable batteries. This has changed over the last few years with the development of the lithium ion battery, which is now used in some electric vehicles.

Lithium ion batteries

Lithium ion batteries should not be confused with lithium metal batteries. Lithium–ion batteries are secondary cells, able to be recharged, while lithium metal batteries are primary cells.

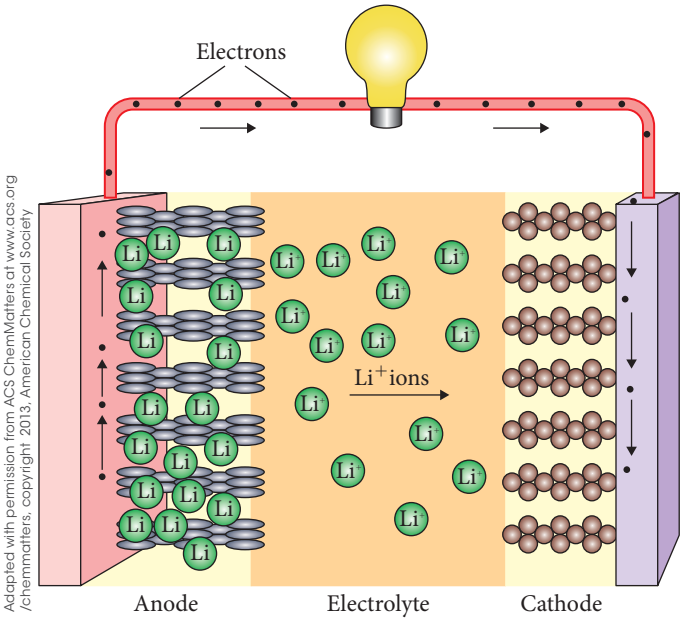
The first lithium ion batteries were commercialised by Sony in 1991 and their use has grown exponentially since then. This is due to improved chemistry and reduced manufacturing costs.

Between 1994 and 2001, the manufacturing costs for lithium ion batteries decreased by a factor of five and have continued to decrease since that time. Lithium ion batteries are used for battery packs for cordless drills, mobile phone batteries and, more recently, in electric cars.

The lithium ion battery has the same components as all batteries – an anode, a cathode and an electrolyte. However, similarly to the lead–acid battery, the electrodes are generally referred to in terms of their polarity. The electrolyte is a non-aqueous lithium salt such as lithium hexafluorophosphate ($LiPF_6$). The positive electrode is coated with a lithium metal oxide such as lithium cobalt oxide ($LiCoO_2$). The negative electrode is made of graphite. Since graphite has a layered structure, lithium atoms are **intercalated** in the graphite. The reactions for the lithium ion batteries are a little more complicated than those seen previously. The reactions during discharge are:

- Negative terminal $Li_xC_6 \rightarrow C_6 + xLi^+ + xe^-$ (where $x = 1$ or 0)
- Positive terminal $Li_{(1-x)}CoO_2 + xLi^+ + xe^- \rightarrow LiCoO_2$ (where $x = 1$ or 0)

When the batteries are attached to a recharger, the reactions are reversed.



◀ **Figure 3.11**
A lithium ion battery contains a graphite anode (left), a lithium cathode (right) and a liquid electrolyte. The battery produces electricity when the lithium atoms in the anode donate their electrons (through the external circuit) to the cobalt oxide (brown spheres) at the cathode.

WOW

Amy Prieto and her improved lithium ion battery

Amy Prieto is an Associate Professor at Colorado State University. She has led a team to develop a lithium ion battery that is 1000 times faster and lasts 10 times longer than existing lithium ion batteries. The important difference is that Prieto's battery uses an anode constructed of nanowires, so small that 10000 of them have the same diameter as a human hair. The use of nanowires significantly increases the surface area of the anode. Nanowires utilising copper antimonide (Cu_2Sb) have been trialled. These are coated with a very thin layer of electrolyte. Some of the improvements from this technology are that Cu_2Sb is stable and heat resistant, so the battery does not overheat. The electrolyte consists of a non-toxic chemical, unlike some currently in use in lithium ion batteries.



▲ **Figure 3.12**
Amy Prieto with part of her revolutionary lithium ion battery

AMY PRIETO, COLORADO STATE UNIVERSITY

Watch this video, which features Amy Prieto discussing the purpose of her work and the importance of developing an effective team.

ACTIVITY 3.6

DIFFERENT TYPES OF LITHIUM ION BATTERIES

Aim

To compare the chemistry and uses of different types of lithium ion batteries

What to do

1 Identify three other types of lithium ion batteries.

2 For each of the types of lithium ion batteries, identify the:

- **a** reaction at the negative terminal during discharge.
- **b** reaction at the positive terminal during discharge.
- **c** use(s) or potential use(s).
- **d** advantages and/or disadvantages or limitations of the battery.

WOW

Lithium ion battery technology

Japanese researchers, led by Tohru Suzuki from the National Institute for Materials Science, have found that if all of the grains of lithium cobalt oxide ($LiCoO_2$) at the positive terminal of a lithium ion battery are aligned in a specific orientation, the battery is significantly more efficient than when the $LiCoO_2$ is randomly orientated. This is due to the lithium ions having a greater access to the lattice and hence movement into and out of the lattice during discharge and recharge is improved.

Comparison of batteries

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126) AC

Batteries have different uses because of their different properties. To determine the most appropriate battery for a particular use, you need to consider its properties.

The lead–acid battery was the first rechargeable battery to be used. It produced a larger voltage than the primary cells available at the time. It was also reasonably cost-effective to produce. It has been deemed the most appropriate for use in vehicles for over a hundred years. However, it is not suitable for small appliances because it is so large. Lead is one of the most dense metals, so the battery is also very heavy.

Some of the important properties of batteries are given below.

Voltage is commonly used to compare batteries. Voltage is a measure of the energy released per unit of charge. So a larger voltage indicates that more energy is released per unit of charge. The lithium ion cell has a voltage of 3.6 V while a lead–acid cell has a voltage of 2 V.

Batteries convert chemical energy to electrical energy. Energy is generally measured in joules (J); however, with batteries we tend to talk about power – the rate at which energy is used.

$$\text{Power} = \frac{\text{energy}}{\text{time}}$$

When the unit of energy is the joule (J) and the unit of time is the second (s), the unit of power is the watt (W). The equation above can be rearranged to make energy the subject.

$$\text{Energy} = \text{power} \times \text{time}$$

Hence, 1 J is equivalent to 1 W s.

Household and industrial appliances usually operate for long periods of time, so the energy used is generally reported in watt hours or kilowatt hours (kWh) rather than watt seconds. An important property when comparing batteries is **energy density**. This is the energy released per unit mass or per unit volume of the battery, generally reported as watt hours per kilogram ($Wh\,kg^{-1}$) or watt hours per litre ($Wh\,L^{-1}$). The energy density for the lead–acid cell is 30–50 $Wh\,kg^{-1}$, while the energy density for the lithium ion battery described above is 150–190 $Wh\,kg^{-1}$. This is one of the main reasons why lithium ion batteries are now being trialled in electric vehicles.

Another property used to compare batteries is the cycle life. Lithium ion batteries can be recharged about three times more than the lead–acid batteries before the battery needs to be replaced.

Disposal of batteries is also a consideration. Batteries should not be disposed with household waste. Most refuse recovery companies have special collection facilities for batteries.

WOW

Disposal of batteries

In Australia, nearly 70000 tonnes of lead–acid batteries are disposed of each year. Lead is a toxic metal and sulfuric acid is corrosive. Ninety-nine per cent of the battery components can be extracted and used in the manufacture of new batteries.

ACTIVITY 3.7

RECHARGEABLE BATTERIES

Aim

To research nickel–cadmium and nickel metal hydride batteries and compare them to lithium ion batteries

What to do

1 Research the nickel–cadmium (NiCd) battery, including the:
   - **a** reaction at the negative terminal during discharge.
   - **b** reaction at the positive terminal during discharge.
   - **c** electrolyte used.
   - **d** properties, e.g. voltage, energy density.
   - **e** advantages and disadvantages or limitations.

2 Research the nickel metal hydride (NiMH) battery, including the:
   - **a** reaction at the negative terminal during discharge.
   - **b** reaction at the positive terminal during discharge.
   - **c** electrolyte used.
   - **d** properties, e.g. voltage, energy density.
   - **e** advantages and disadvantages or limitations.
   - **f** why the NiMH battery has replaced the NiCd battery.

3 Compare the properties of nickel–cadmium, nickel metal hydride and lithium ion batteries and justify why lithium ion batteries are gradually replacing these other batteries.

ACTIVITY 3.8

BATTERIES – IMPACT ON OUR WORLD

Aim

To evaluate the impact of batteries on our way of life and the environment

What to do

1 Summarise the properties and uses of the different types of primary and secondary cells, using information in the text and at least three other sources.

2 The Prime Minister is seeking the views of young people about the world in which they live. You have been asked to give your views about the use of batteries and how they have impacted on the way we live our lives and the environment. The Prime Minister would like you to propose ideas about how we can more sustainably use our resources so that they are also available for future generations. Use your knowledge of batteries to develop your arguments.

Vanadium redox battery

For further discussion of oxidation states, refer to Chemistry section 3.6, page 218.

So far, we have looked at batteries that have been used in vehicles and small appliances such as watches, cameras and mobile phones. The vanadium redox battery is a larger battery, which can store large quantities of energy. Its typical storage capacity is in the megajoule range, rather than the kilojoule range of many other batteries. It can be used to supplement the supply of electricity from solar or wind sources so that supply is more constant and reliable.

The vanadium redox battery is a secondary cell. It consists of two compartments with a porous membrane between them. Each compartment contains a different vanadium solution. Vanadium is a transition metal, which means that it exists in multiple oxidation states. The vanadium solutions in each compartment have different oxidation states. The compartments are connected to an external circuit via inert metal electrodes.

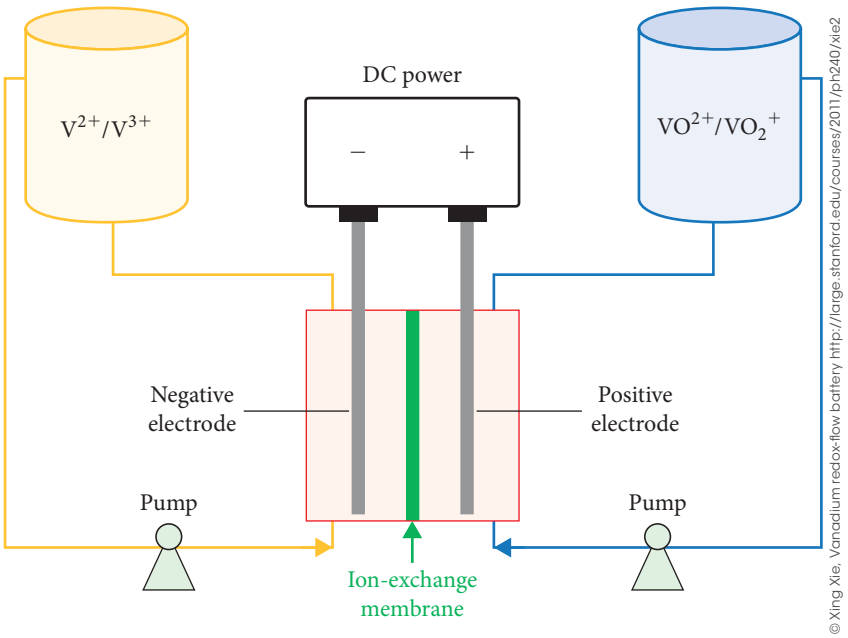


Figure 3.13 ▶ Schematic diagram of the vanadium redox battery

International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region. (ACSCH087 and ACSCH125)

During discharge, the following reactions occur.

- Negative terminal $V^{2+}(aq) \rightarrow V^{3+}(aq) + e^-$
- Positive terminal $VO_2^+(aq) + e^- + 2H^+(aq) \rightarrow VO^{2+}(aq) + H_2O(l)$



University of New South Wales

◀ **Figure 3.14**
Professor Maria Skyllas-Kazacos and her research team at the University of New South Wales developed the vanadium redox battery.

EXPERIENCE MATTERS

Watch this video in which Dr Maria Skyllas-Kazacos explains how the vanadium redox battery works.

GO WITH THE FLOW

Watch this video interview with Dr Maria Skyllas-Kazacos about the vanadium redox battery, including the challenges of moving from research to commercialisation.

The battery can be recharged by passing an electric current through it and reversing the flow of the solutions. The amount of charge stored in the battery is dependent on the size of the storage tanks for each of the solutions. These can be placed underground for economical use of land.

The vanadium redox battery was developed in the early 1980s in the School of Chemical Engineering and Industrial Chemistry (CEIC) at the University of New South Wales. It was patented in 1986. The research team was led by Professor Maria Skyllas-Kazacos. Vanadium redox batteries are currently used in Australia, Italy, Japan, South Africa, Kenya, Indonesia, the United States, Portugal and the Netherlands. Research is continuing with both generation 2 and generation 3 vanadium redox batteries to improve the energy density of the battery. The University of New South Wales, in collaboration with Nanyang Technological University in Singapore, is working to develop generation 2 vanadium redox batteries that will have improved energy density and operate over a larger temperature range.

ACTIVITY 3.9

MARIA SKYLLAS-KAZACOS

Aim

To work as a member of a team to put together an episode of the TV program *This is Your Life* for Maria Skyllas-Kazacos

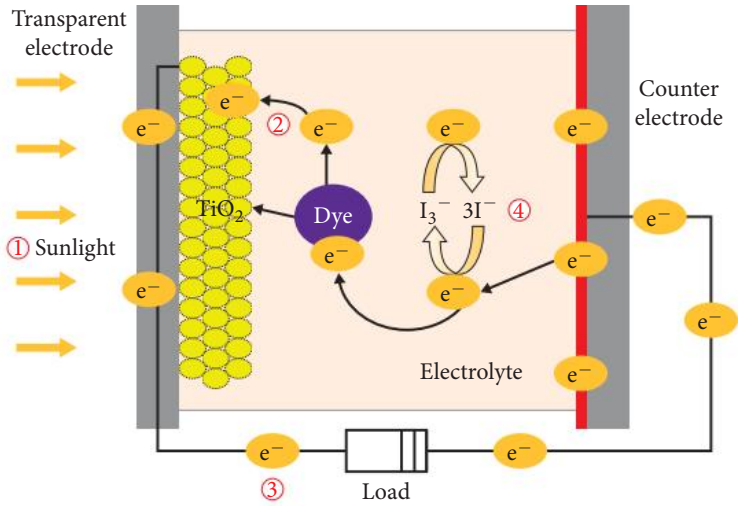
What to do

1. Use a variety of sources to identify the events in the life, and work, of Maria Skyllas-Kazacos.
2. Categorise the events in terms of their significance – events that must be included in the TV program, events that could be included if there is time and events that will end up on the cutting-room floor.
3. Develop the storyboard for one or two scenes for the TV program.
4. Video one or two scenes for the TV program.

Solar cells

Solar cells are photovoltaic devices that use materials to convert solar energy to electrical energy. Traditionally materials have been composed of silicon chips that have been doped with small amounts of either phosphorus or boron. The science involved with many of these photovoltaic devices is very different from that for galvanic cells. In 1991, Michael Grätzel and his research group at the Swiss Federal Institute of Technology developed the Grätzel solar cell. The Grätzel solar cell is a dye-sensitive solar cell (DSC). It consists of two conducting glass plates. One glass plate is coated with titanium dioxide (TiO_2) onto which a dye has **adsorbed**. The other

Figure 3.15 ▶
Schematic diagram of the Grätzel solar cell



Moon, J. et al. (2012) 'Forecasting a change in technology: are Dye-sensitised Solar Cells a source of ubiquitous energy?', *International Journal of Technology, Policy and Management*, 12 (2/3), pp. 177–94. Reproduced with permission of Inderscience Publishers via Copyright Clearance Center.

glass plate is coated with graphite. An electrolyte of potassium iodide and iodine is sandwiched between the two electrodes.

The mechanism for the Grätzel solar cell is outlined in Figure 3.15.

1 Sunlight passes through the titanium dioxide layer and strikes the dye molecules adsorbed to the titanium dioxide layer where the electrons are excited.
2 The excited electrons are emitted from the dye and gather at the titanium dioxide-coated electrode.
3 The free electrons then move through the external circuit to the positive, graphite-coated plate electrode.
4 The dye is regenerated by the transfer of electrons from the iodide electrolyte. The iodide is oxidised to form triiodide (I_3^-). The free electrons from the external circuit then reduce the triiodide to iodide. This step involves electrochemistry. The dye is reduced while iodide is oxidised.

Overall, all materials are regenerated at the end of each cycle. Hence, it can continue to operate indefinitely. Grätzel solar cells are very thin and almost transparent. They can be used as watch faces to generate enough power to run the watch. There is research into using them for building materials where they could generate some of the electricity for the house.

Fuel cells

For more discussion on the chemistry of a fuel cell, refer to Chemistry section 5.5, page 264.

Fuel cells are like galvanic cells since they convert chemical energy directly into electrical energy without the intermediate production of heat energy and mechanical energy that occurs with the combustion of fossil fuels. However, in traditional galvanic cells, the reactant chemicals are eventually used up. When this occurs, the batteries are replaced or recharged. Fuel cells have external supplies of fuel, usually hydrogen, and an oxidiser, oxygen. The fuel cell can operate as long as it has supplies of these chemicals. A fuel cell is refuelled instead of being replaced or recharged. Fuel cells have the same components as batteries, namely anode, cathode and electrolyte. However, unlike batteries, fuel cells do not store energy.

Fuel cells are used by a number of multinational corporations to supplement electricity from the power grid. There is also much interest in their potential use in cars, buses, boats and planes. Although there are pilot programs occurring in each of these industries, none has yet reached commercialisation. This is partly due to the lack of facilities for refuelling these vehicles.

There are many different types of fuel cells. They may have different electrolytes, catalysts, operating temperatures and efficiencies. Some of the common types of fuel cells are:

- proton exchange membrane fuel cell (PEM)
- alkaline fuel cell (AFC)
- direct methanol fuel cell (DMFC)
- phosphoric acid fuel cell (PAFC)

- molten carbonate fuel cell (MCFC)
- solid oxide fuel cell (SOFC).

In most fuel cells except the direct methanol fuel cell, the following reactions occur:

- Anode $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$
- Cathode $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

In the direct methanol fuel cell, the anode reaction is:

$$CH_3OH(l) + H_2O(l) \rightarrow 6H^+(aq) + 6e^- + CO_2(g)$$

One of the main issues related to fuel cells is the sourcing of hydrogen. Hydrogen has to be extracted from other sources, such as the electrolysis of water or re-forming of hydrocarbons. However, these processes require the input of significant amounts of energy so the economic viability is questionable. Re-forming of hydrocarbons also produces carbon dioxide, which continues to contribute to climate change. However, the efficiency of the fuel cell is greater than the efficiency of the combustion of fossil fuels, so less carbon dioxide is produced.

The steam re-forming process for natural gas involves a nickel catalyst and temperatures in excess of 700°C.

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

The carbon monoxide undergoes a further reaction to increase the yield of hydrogen.

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

ACTIVITY 3.10

COMPARISON OF FUEL CELLS

Aim

To compare the chemistry and properties of the different types of fuel cells

What to do

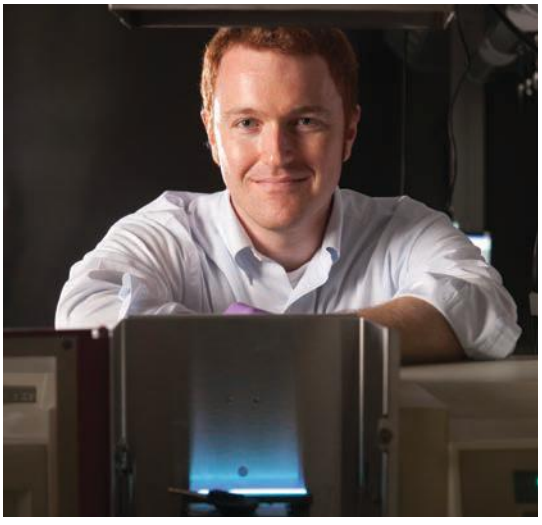
1. For each type of fuel cell, research the sources of fuel, catalyst used, electrolyte used, operating temperature and efficiency.
2. Evaluate the data to make a judgement about the fuel cell that you think shows the most potential for further development. Justify your decision.

Latest developments in fuel cell technology

One of the greatest challenges for the further development of fuel cells is the supply of the hydrogen fuel for the cell. In many existing cells, platinum is the catalyst of choice for this process. However, platinum is very expensive, which limits the commercial viability of fuel cells. Much research is being conducted in this area.

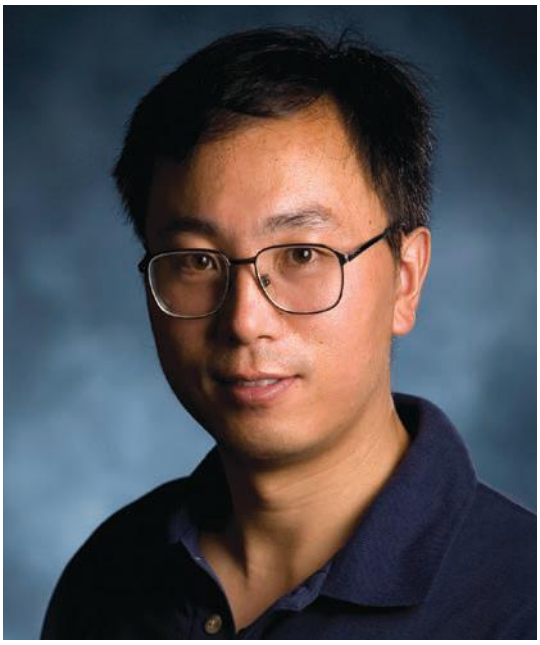
One area of research is the development of solar fuel cells, fuel cells that utilise the Sun's energy. In the past, indium tin oxide has been used to catalyse the decomposition of water to produce hydrogen gas. However, indium is not very abundant in the Earth's crust; it is about as abundant as silver. Therefore, this is a very expensive process, which is not likely to be cost-effective or economically viable when scaled up to commercial levels.

Scientists at Duke University in the United States, led by Assistant Professor Ben Wiley, have found that copper nanowire catalysts can assist with the decomposition of water to produce hydrogen gas. The advantages of using copper nanowires instead of indium tin oxide is mainly related to the greater abundance, and hence availability, of



Benjamin J. Wiley, Department of Chemistry/Duke University

▲ **Figure 3.16**
Assistant Professor Ben Wiley and his team have found a way to use copper nanowires in solar fuel cells to catalyse the decomposition of water to produce hydrogen.



Jiming Bao/University of Houston

Figure 3.17 ▲
Assistant Professor Jiming Bao and his team of scientists have discovered how to use nanoparticles of cobalt oxide to catalyse the decomposition of water.

copper. Copper is 1000 times more abundant than indium and 100 times cheaper. The copper nanowires are coated with cobalt or nickel, which acts as the catalyst. These enable seven times more sunlight to pass through than with the indium tin oxide. However, further challenges still remain. The use of the copper nanowires enables water oxidation to occur. Further research is required to find ways of harnessing the electrons produced to reduce water to hydrogen.

Scientists at the University of Houston, led by Assistant Professor Jiming Bao, have used nanoparticles of cobalt oxide to catalyse the decomposition of water using light to produce hydrogen gas and oxygen gas. This process happens almost immediately once the catalyst is present. This project is an example of the importance of global collaboration to address issues facing our world. It is also an example of public companies partnering university researchers. Collaborators in this project included researchers from the University of Houston, Sam Houston State University, the Chinese Academy of Sciences, Texas State University, Carl Zeiss Microscopy LLC and Sichuan University. This may lead to the availability of hydrogen fuel for fuel cells, without the need to extract it from fossil fuels.

To move from a small-scale research project to a large-scale commercialised project requires a significant investment. The International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE) was established in 2003. Its purpose is to work towards the commercialisation of hydrogen and fuel cell technology, which will have benefits for both society and the environment. Australia is one of 18 partner countries involved in this organisation. This organisation facilitates opportunities for international partnerships for both research and commercialisation related to hydrogen and fuel cells.

International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region. (ACSCH087 and ACSCH125) AC

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126) AC

BUG-POWERED BATTERIES

Watch this video of Dr Basil Singer interviewing Professor Derek Lovley about his microbial fuel cell.

Microbial fuel cells

Scientists are continually looking for ways to develop new energy sources that are sustainable over the longer term. However, economic viability is also important. Microbial fuel cells are one area of current research. Professor Derek Lovley from the University of Massachusetts has conducted research on the bacteria *Geobacter sulfurreducens*. It produces tiny electrical currents. Lovley uses two pieces of graphite, each about 0.5 cm thick, as the terminals. The terminals are connected by a waterproof wire. One of the terminals is placed in the mud at the bottom of a body of water. The bacteria grow naturally on the surface of the metal, producing a **biofilm**. The other terminal is placed in the water above the mud. The bacteria oxidise the acetate present in the decaying organic matter in the mud to form carbon dioxide and hydrogen ions:

$$CH_3COO^-(aq) + 2H_2O(l) \rightarrow 2CO_2(g) + 7H^+(aq) + 8e^-$$

The electrons are accepted by the graphite and travel through the external circuit to the positive terminal where oxygen dissolved in water is reduced:

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

Lovley's microbial fuel cell is only producing very low currents – about 65 mA m^{-2} of electrode surface. Hence, very large electrode surface areas are needed to produce larger quantities of electricity. The technology is not very practical for development for larger scale applications. The main advantage of bacterial fuel cells is that they are carbon neutral. Although these fuel cells produce carbon dioxide, this would have been produced by the bacteria decomposing the organic matter. The only difference is that the electricity produced by the bacteria is being utilised. It is not contributing extra carbon dioxide to the atmosphere as occurs when fossil fuels undergo combustion reactions.

The limiting step in Lovley's microbial fuel cell is the transfer of the electrons from the *Geobacter* to the graphite electrode. Further research is being conducted on ways to improve this process.

WOW

Uranium clean-up

Professor Derek Lovley is also looking at the use of the bacteria *Geobacter* for the removal of uranium from groundwater. The uranium acts as an electron acceptor, reducing the uranium from soluble uranium(VI) to insoluble uranium(IV). The aim is to precipitate the uranium out of surface waters before it gets into the groundwater.

The fuel for microbial fuel cells can be as diverse as leftover food, sewage, manure or even human waste – any natural organic material. If the fuel consists of plant-based material, then the bacteria will consume the sugar in the leaves and produce carbon dioxide, hydrogen ions and electrons.

In this case, the anode reaction becomes:

$$C_{12}H_{22}O_{11} + 13H_2O(l) \rightarrow 12CO_2(g) + 48H^+(aq) + 48e^-$$

The electrons then travel through the external circuit to the cathode where the electrons react with hydrogen ions and oxygen to produce water.

$$12O_2(g) + 48H^+(aq) + 48e^- \rightarrow 24H_2O(l)$$

A research group from Harvard University's School of Engineering and Applied Sciences has decided to trial microbial fuel cells in two projects in Africa – one in Namibia, the other in Tanzania. They set up a company, Lebone Solutions. Using a grant from the World Bank as well as funds from private investors, they are trialling the use of microbial fuel cells to provide the residents with electricity.

Scientists from the Advanced Water Management Centre at the University of Queensland are also involved in research related to microbial fuel cells. However, they are not looking to use the electricity externally; they are looking at the treatment of wastewater. In one project, the useful chemical caustic soda, sodium hydroxide, is being extracted from wastewater from industrial processes. It is used for adjusting pH, as a cleaning agent and in the pulp and paper, textiles and food processing industries. Dr Korneel Rabaey is hoping that companies will now be able to recover the caustic soda from their wastewater and re-use it in cleaning processes and reprocess again, instead of discharging it into the environment. Salinity is a major environmental problem in Australia.

In a traditional microbial fuel cell, the hydrogen ions move to the cathode and react with oxygen to form water. In the caustic soda-producing microbial fuel cell, the sodium ions move to the cathode where the oxygen is partially reduced to form hydroxide ions; hence, sodium hydroxide is produced. Although the composition of wastewater varies from site to site, modelling suggests that if wastewater contains about 3 kg m^{-3} of organic matter and 2 kg m^{-3} of sodium, then about 0.5 kg would be used to produce 2.5 kg of sodium hydroxide. This would remove about 1.44 kg m^{-3} from the stream of wastewater. This process is also cost-effective, so it has both economic and environmental benefits.

The Advanced Water Management Centre has also been collaborating for over 10 years with the Beijing University of Technology to develop processes that enable more sustainable wastewater treatment and water recycling processes.

CHAPTER SUMMARY

- Many current sources of energy for our everyday activities involve the transformation of chemical energy to heat energy. However, redox (oxidation–reduction) chemistry involves transforming chemical energy to electrical energy, and, in some cases, the reverse.
- Electrochemistry involves both galvanic cells and electrolytic cells. Galvanic cells involve the transformation of chemical energy to electrical energy while electrolytic cells involve the transformation of electrical energy to chemical energy.
- Galvani, Volta, Davy and Faraday made significant contributions to our understanding of electrochemistry. Galvani and Volta contributed to our understanding of what are now known as galvanic cells. They had conflicting views on the origins of electricity. This is a good example of the way that ideas in science change as more evidence becomes available. Davy and Faraday contributed to our understanding of electrolysis.
- Batteries can be either primary cells or secondary cells. Primary cells are disposable batteries; they are not able to be recharged. The Daniell cell, Leclanché cell (dry cell), alkaline batteries, lithium batteries and silver oxide batteries are examples of primary cells. The lead–acid, lithium ion, nickel–cadmium and nickel metal hydride batteries are all examples of secondary cells.
- Different batteries have different uses. It is important to look at the properties of different batteries to identify the battery most suitable for a specific purpose. Properties that need to be considered include voltage, energy density (which is related to the mass and size of a battery), cost, method of disposal, whether it is rechargeable and, if so, the number of recharge cycles that are possible before it has to be replaced.
- Newer technologies related to electrochemical cells as sources of energy include the vanadium redox battery that was developed in Australia, dye-sensitised solar cells, fuel cells and microbial fuel cells. Each of these technologies is more environmentally friendly than existing primary and secondary cells. However, further development is needed to make them economically viable enough to replace more traditional batteries. or the use of fossil fuels, especially in larger projects such as powering motor vehicles.
- The development of newer technologies involves scientists working collaboratively within specific institutions and on a more global scale to build on each other's work. Funding for science projects is sourced from governments, global companies and private donations. Universities in developed nations are developing projects to enhance the living conditions for people in developing nations.

CHAPTER GLOSSARY

adsorb when atoms, ions or molecules adhere to a surface

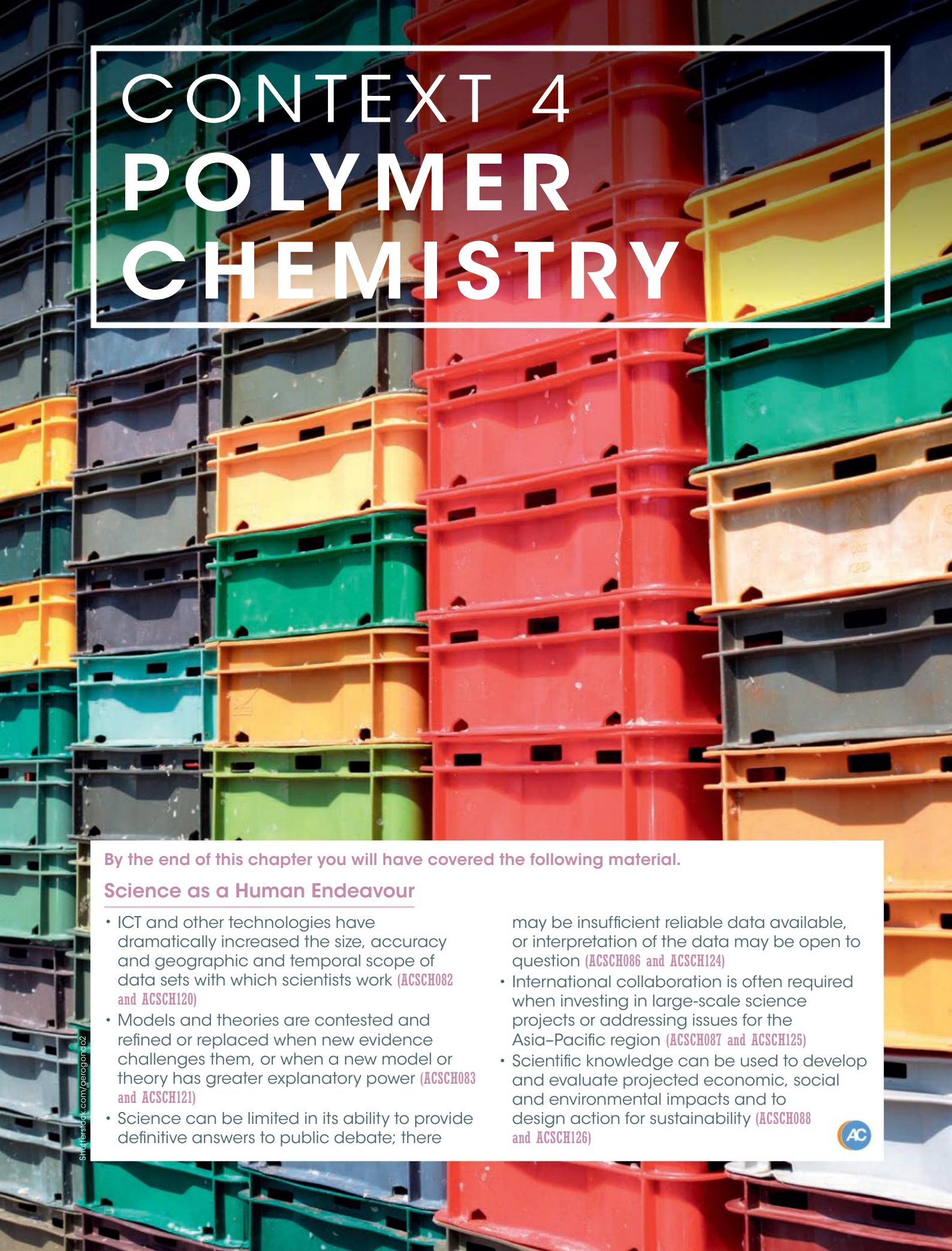
biofilm a stable colony of bacteria coating a material

brine a salt solution, usually sodium chloride

energy density the energy released per unit mass or per unit volume of the battery

intercalated when one substance, lithium in the case given, is inserted between the layers of graphite

CONTEXT 4
POLYMER CHEMISTRY



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By the end of this chapter you will have covered the following material.

Science as a Human Endeavour

- ICT and other technologies have dramatically increased the size, accuracy and geographic and temporal scope of data sets with which scientists work (ACSCH082 and ACSCH120)
- Models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory power (ACSCH083 and ACSCH121)
- Science can be limited in its ability to provide definitive answers to public debate; there may be insufficient reliable data available, or interpretation of the data may be open to question (ACSCH086 and ACSCH124)
- International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region (ACSCH087 and ACSCH125)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCH088 and ACSCH126)

Contextual story – Polymer chemistry

- Plastics are polymers
- Recycling plastics – where do they go?
- Polymers – where do they come from?
- Thirsty polymers
- Conducting polymers
- Clothes from plastic bottles
- Nylon – a polyamide imitating nature
- Kevlar – fabric of steel
- Green polymers

Chemical understanding

- Polymers are organic compounds which are made from a variety of different staring materials through different synthesis processes.
- The properties of polymers are determined by a number of different factors.
- Functional groups are important in the synthesis of polymers and their properties.
- The structures of polymers both natural and synthetic may be determined by different analytical techniques.
- Polymers may be produced using different starting material, which makes them more environmentally friendly.

Investigations

Chapter 4

- Activity 4.1 Properties of different plastics
- Activity 4.3 Environmental impact of plastics
- Activity 4.7 Health concerns
- Activity 4.8 How strong is Teflon?
- Activity 4.11 Time-release aspirin
- Activity 4.12 Nylon vs polyester
- Activity 4.14 Cornstarch vs polystyrene packaging
- Activity 4.15 Biopolymers

Chapter 6

- Experiment 6.1 Comparing reactivities of alkanes and alkenes
- Experiment 6.2 Distinguishing between primary, secondary and tertiary alcohols
- Experiment 6.3 Preparation of some esters

Chapter 7

- Experiment 7.1 Investigating crystalline and amorphous packing in polymer chains
- Experiment 7.1 Identifying plastics by their density

Science as a Human Endeavour (SHE)

- ICT and other technologies have dramatically increased the size, accuracy and geographic and temporal scope of data sets with which scientists work (ACSCH082 and ASCH120)
- Models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory power (ACSCH083 and ACSCH121)
- Science can be limited in its ability to provide definitive answers to public debate; there may be insufficient reliable data available, or interpretation of the data may be open to question (ACSCH086 and ACSCH124)
- International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region (ACSCH087 and ACSCH125)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCH088 and ACSCH126)

Science Understanding (SU)

- Organic molecules have a hydrocarbon skeleton and can contain functional groups, including alcohols, carboxylic acids, esters, amines and amides (ACSCH127)
- Each class of organic compounds displays characteristic chemical properties and undergoes specific reactions based on the functional groups present; these reactions, including acid–base and oxidation reactions, can be used to identify the class of the organic compound (ACSCH128)
- Organic materials including proteins, carbohydrates and synthetic polymers display properties including strength, density and biodegradability that can be explained by considering the primary, secondary or tertiary structures of the material (ACSCH129)
- Organic molecules, including polymers, can be synthesised using addition and condensation reactions (ACSCH136)
- Data from analytical techniques, including mass spectrometry, X-ray crystallography and infrared spectroscopy, can be used to determine the structure of organic molecules, often using evidence from more than one technique (ACSCH130)
- Designing chemical synthesis processes involves constructing reaction pathways that may include more than one chemical reaction (ACSCH132)
- Designing chemical synthesis processes includes identifying reagents and reaction conditions in order to maximise yield and purity of product (ACSCH133)
- Green chemistry principles include the design of chemical synthesis processes that use renewable raw materials, limit the use of potentially harmful solvents and minimise the amount of unwanted products (ACSCH135)

Science Inquiry Skills (SIS)

- Identify, research, construct and refine questions for investigation; propose hypotheses; and predict possible outcomes (ACSCH112)
- Design investigations, including the procedure/s to be followed, the materials required, and the type and amount of primary and/or secondary data to be collected; conduct risk assessments; and consider research ethics (ACSCH113)
- Conduct investigations, including using organic synthesis methods and collating data from chemical analyses, safely, competently and methodically for the collection of valid and reliable data (ACSCH114)
- Interpret a range of scientific and media texts, and evaluate processes, claims and conclusions by considering the quality of available evidence, including confidence intervals in secondary data; and use reasoning to construct scientific arguments (ACSCH116)
- Select, construct and use appropriate representations, including physical, virtual and graphical models of primary, secondary and tertiary structures, structural formulas, chemical equations, systematic nomenclature (using IUPAC conventions) and spectra, to communicate conceptual understanding, solve problems and make predictions (ACSCH117)
- Select and use appropriate mathematical representations to solve problems and make predictions (ACSCH118)
- Communicate to specific audiences and for specific purposes using appropriate language, nomenclature, genres and modes, including scientific reports (ACSCH119)

Introduction

Polymers are everywhere in the modern world. They can be natural, such as carbohydrates (e.g. cellulose), proteins (e.g. silk) and natural rubber, or they can be synthetic.

Synthetic polymers, usually referred to as **plastics**, are fundamental to our lifestyle. They are found in packaging, adhesives, clothes, medical devices and so many other materials that it would be impossible to list them all. These materials have revolutionised sports equipment and been responsible for major advances in electronic technology. The amount of polymers used in the aviation industry has doubled in the last decade because they can be engineered to offer strength and lightness.

From an early age, you have been surrounded by plastic – plastic toys, plastic containers, plastic bags, even non-stick coating on pans, chewing gum and Lycra in clothes are made from plastic. The development of plastics has only occurred in the last 70 years or so and they have only been used on a massive scale over the last 60 years. At this moment, you are probably using a number of different materials that did not exist even 10 years ago, particularly in electronics technology.



Deb Smith

◀ **Figure 4.1**
Some of the many plastics found around the home

At least some of your clothing probably contains synthetic fibres. Your pen is made mainly of plastic, your calculator has a plastic case and so does your mobile phone and computer. All DVDs are made of plastic and so are their containers. Your sports shoes alone probably consist of six or more different kinds of plastic, including the sole, the padding, the upper, the laces and even the lace tips.

Plastics are amazing materials, coming in every shape, size and colour and with every material property you could think of – strong, flexible, elastic, hard, ductile, transparent, slippery, brittle, to name a few. As chemists develop new plastics, the variety of properties and uses expand dramatically.

However, the widespread distribution and use of plastics has not been without cost. There are two main problems that need to be considered as plastic use continues to escalate. One is what to do with plastic articles after we have finished using them and the other is to find a new source of the raw material of plastic manufacture as the current one runs out.

PLASTICS TIMELINE

Watch a video showing the timeline of plastics from the 1820s until today.

Plastics are polymers

The term 'plastic' is applied to a wide range of materials with a wide range of properties and applications. Technically, 'plastic' means 'deforms permanently when subjected to a force' but as a general term it has come to be used for a range of synthetic substances more appropriately known as polymers. Polymers are large molecules made up of many repeating units. *Poly* is from the Greek for 'many' and *meros* is from the Greek for 'part'. Common names or brands for these polymers include rayon, nylon, Lycra, polyurethane, Teflon, Styrofoam and PVC.

All plastics are polymers but not all polymers are plastics. Polymers are also produced in profusion by nature. Some of the many natural polymers are cellulose, cotton and rubber found in plants; wool, skin and hair are proteins from animals; DNA found in all living things is another natural polymer. Chemists have copied many of these natural polymers, often making small changes to them. Many synthetic polymers were originally produced as substitutes for expensive naturally occurring materials or to improve on natural polymers. Today, chemists are going back to the original materials and looking at how to incorporate them into new polymers or as a source of building blocks for new polymers.

WOW

Inspiration from mussels

Researchers from Pennsylvania State University and the University of Texas-Arlington have incorporated the chemical structure from a mussel's adhesive protein into the design of an injectable synthetic polymer called iCMBA (Injectable Citrate-based Mussel-inspired Biodegradable Adhesive). These bio-adhesives provide 2.5–8.0 times stronger adhesion in wet tissue conditions than current products.

iCMBA polymers stop bleeding instantly, facilitate wound healing, close wounds without the use of sutures and offer controlled degradation. Additionally, the synthesis of the material can be controlled to produce variations that will degrade over different lengths of time.

Other predicted surgical applications include replacing sutures and staples and adhering tissue grafts used to treat ulcers, hernias and burns.



Biophoto Associates/Photo Researchers/Getty Images

Figure 4.2 ▶
Mussels anchor themselves by strong, flexible byssal threads.

A good way to begin your study of polymers is by collecting a range of plastics you come into contact with almost every day and investigating the properties of these common materials (Figure 4.3).



Deb Smith



Deb Smith

▲ **Figure 4.3** Products made from six common types of polymer along with their plastics identification code

ACTIVITY 4.1

PROPERTIES OF DIFFERENT PLASTICS

a Collect a variety of plastic items from your home – plastic bags, soft-drink bottles, milk bottles, take-away food containers and whatever happens to be on hand.

The plastics used to make the items will have different properties related to their use. You are to test and compare some of the properties of these plastics.

b Decide on some properties to investigate, e.g. colour, flexibility, elasticity, hardness, water absorbency, ease of melting and heat shrinkage. You will need to devise tests for these properties, being sure to control as many variables as possible.

Warning: Burning polymers give off toxic fumes, so do not expose your sample directly to a flame unless it is done in a fume cabinet. To determine melting, you could use hot water or a nail heated in a Bunsen burner or place in an oven.

c Draw up a table to record your results.

d Use your test results to identify items that are made from the same material.

e Compare the properties of the different plastics and relate the properties to the use.

In investigating the properties of plastics in Activity 4.1, you probably found that they exhibited a wide range of properties. The plastic that makes up most soft-drink and water bottles is transparent and has moderate hardness and flexibility, while a Styrofoam cup is white, opaque, light, soft and easily torn. Today, more than 60 000 plastics are known and you investigated only a very few.

If so many plastics are being used, why are we not drowning in them? Or are we? Let's consider this.

International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region. (ACSCH087 and ACSCH125)

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126) AC

Recycling plastics – where do they go?

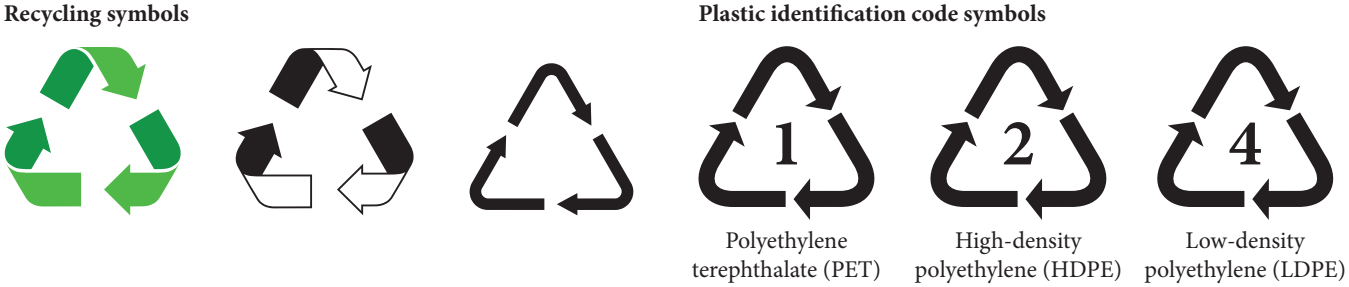
By the 21st century, the volume of plastics on the world market exceeded the total volume of metals. Plastic production worldwide now exceeds 300 million tonnes a year. The amount of plastic manufactured in the first 10 years of this century equals the total produced for the entire last century. Only about 10 per cent of that is recycled. Australia is one of the highest waste producers in the world, currently ranked in the top five waste-producing nations.

Australia contributes almost 1.3 million tonnes to plastic production, which is more than 71 kg for every person. Packaging is the largest market for plastics with approximately 376 000 tonnes used per year, accounting for over a third of the consumption of raw plastic materials – Australians use 15 253 tonnes of soft-drink bottles, 30 000 tonnes of milk bottles and 6.9 billion plastic bags every year.

While plastic packaging provides excellent protection for the product and is lightweight compared to metal or cardboard, it is proving to be a major environmental problem. In the past, more than one-third of the plastic consumed in Australia was destined for landfill but today many local councils have recycling facilities for plastic materials.

Six polymeric materials account for 66 per cent of all plastics used, but not all of these can be recycled. Since most plastics are incompatible when mixed together, the different types of plastics need to be separated before they can be recycled. To help identify plastics, manufacturers use a plastics identification code, which is normally stamped on all products.

▼ **Figure 4.4**
Recycling symbols and plastic identification codes



Lskywalker/Shutterstock.com; Mafilja Marcius/Shutterstock.com

ACTIVITY 4.2

IDENTIFYING PLASTICS BY THEIR CODE

a Information about the name, properties, uses for the virgin plastic and some uses of the recycled plastic based on the plastics identification code is easily obtained from the web. Either search the internet, using the term 'plastic identification code' or use the weblink to obtain the required information.

b Compare this information with the results of your investigation in Activity 4.1 and name the plastics you tested.

PLASTIC IDENTIFICATION CODE

Visit this website to see a list of plastic identification codes.

It is represented by a triangle with a number inside it. People often get this code confused with the recycling symbol, which is a triangle made up of three arrows with no number inside.

The plastics identification code does not mean the plastic container can be recycled – it identifies the type of plastic the product is made from.

Although all plastic packaging is recyclable, not all is recycled through kerbside recycling schemes. Most councils are able to recycle only the plastic code groups 1, 2 and 3.

If you are unsure what plastic bottles or containers can go into your recycling service, then contact your local council or visit www.RecyclingNearYou.com.au.

Figure 4.5 ▶
Recycling station



Deb Smith

RECYCLING PLASTICS

Watch this video, which shows how plastics are recycled.

Recycling is beneficial for the environment in a number of ways. Apart from reducing the amount of landfill, recycling plastic to make new products is more energy efficient and uses only 30 per cent of the energy required to make the original product. Recycling 1 tonne of plastics can save enough energy to run a refrigerator for a month. It takes 125 recycled plastic milk bottles to manufacture a 140-litre wheelie bin.

As well as saving energy, recycling reduces the amount of raw material needed to produce plastics.

Currently, Australians recycle approximately 23 per cent of plastic packaging products. The majority of the remainder goes into landfill. This is creating a major waste management problem. Plastic debris has accumulated in natural habitats from the poles to the equator with substantial quantities in marine environments.

There is also evidence that plastics are fragmenting in the environment and as a consequence more organisms will begin to ingest these smaller fragments. There is speculation that this will lead to the transfer of toxic chemicals to wildlife.

PLASTIC POLLUTION

Watch this video of plastic pollution in the ocean.

ACTIVITY 4.3

ENVIRONMENTAL IMPACT OF PLASTICS

a Research a significant impact that plastic waste has had on the environment.

b Suggest how scientific knowledge can be used to reduce this problem.

Polymers – where do they come from?

To revise the chemical structure of alkanes and alkenes, refer to Nelson Chemistry Units 1 & 2, *Chapter 3.*

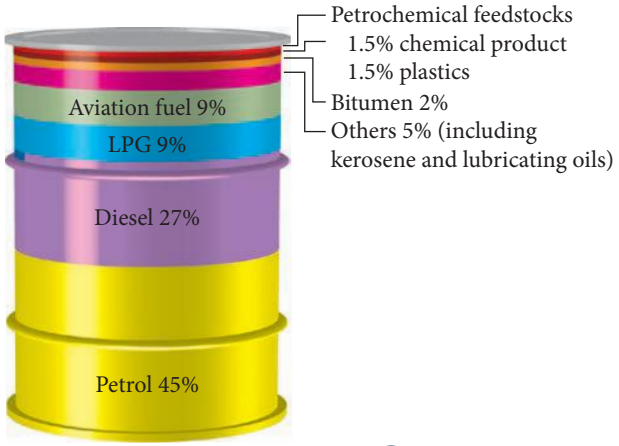
British inventor Alexander Parkes produced the first plastic in 1862 – cellulose nitrate – which could then be converted to various products. He made the cellulose nitrate from wood or cotton and camphor. At the same time an American, John Hyatt, was also experimenting with cellulose nitrate in an attempt to find a synthetic substitute that could replace ivory originally used to make billiard balls and win a $US10 000 prize. He produced a material that he called celluloid and patented it in 1869. Although it was unsuitable for billiard balls, it could be used to make combs, brush handles, photographic film and table-tennis balls. It had the major disadvantage of being highly flammable. Its use boomed until the mid-1920s when other less flammable materials were synthesised.

The first true synthetic polymer was Bakelite, developed by Dr Leo Baekeland in 1907. While celluloid was a natural polymer modified by humans, Bakelite was produced from manufactured chemicals and was unlike anything produced in nature. It is still used to make electrical fittings such as sockets and plugs.

Baekeland's discovery started a scientific and industrial revolution using manufactured chemicals to produce new materials, but it was not until the 1950s that that the most common polymers, nylon, polyethylene, polystyrene and PVC, were manufactured in significant quantities for the general public.

Today, much of the raw material for plastics comes from petroleum (crude oil). You learnt in *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 3 that crude oil is used mainly as a source of fuel for cars, aeroplanes and trains. However, it has also become an important source of chemicals for making new materials, such as plastics, medicines and fertilisers.

▼ **Figure 4.6**
Products made from refining one barrel of crude oil



The refining of crude oil by fractional distillation produces an impressive array of products. Crude oil contains a range of hydrocarbons that vary in size and structure, including straight and branched alkanes, alkenes and cyclic hydrocarbons.

The **petrochemical industry** consumes about 3–5 per cent of the total oil used in the world today. About 95 per cent of all synthetic carbon compounds are derived from compounds produced from petroleum and natural gas.

Research has shown that many of the compounds distilled from crude oil are not ideally suited for the desired applications. The most useful fractions are the lighter ones and so there is a great demand for these. Over half the fractions obtained from crude oil, however, are the heavier, less useful ones.

Oil refineries have developed methods in which fractions containing hydrocarbons of higher molecular mass can be converted into the more useful hydrocarbons of lower molecular mass. The process used is called **catalytic cracking**.

The most widely used starting substance for making polymers is ethene. (The historical name for ethene is ethylene and this historical name tends to be the preferred name and so is more commonly used.) Ethylene is obtained from crude oil, either as a by-product of petrol refining or by the deliberate decomposition or cracking of some of the higher boiling point fractions.



To learn about branched alkanes, alkenes and cyclic hydrocarbons, refer to Chemistry sections 6.2 and 6.3, pages 282 and 292.



To learn about how ethylene is produced by cracking larger hydrocarbon molecules, refer to Chemistry section 7.1, page 328.

Challenging ideas in organic chemistry

Models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory power. (ACSCH087 and ACSCH121) AC

Hermann Staudinger (1881–1965) was a highly respected German organic chemist who had been instrumental in the synthesis of pyrethrins and many other synthetic compounds when he began to challenge traditional thinking and advance new and revolutionary ideas about the existence of macromolecules.

In 1920, he created a stir in the international chemical community when he postulated that materials such as rubber have very high molecular mass and presented several reactions that form high molecular mass molecules by linking a large number of small molecules together by a process he called 'polymerisation'.

While polymers had already been developed from natural materials and the first synthetic polymer, Bakelite, had been produced, the field of polymer chemistry was just beginning to develop.

Staudinger's concept of macromolecules was very challenging to his contemporaries and they were very unwilling to admit to the existence of molecules as large as those proposed by Staudinger. Some scientists were unwilling to admit that molecules could be larger than an individual cell.

To learn how crystallisation is used for chemical analysis, refer to Chemistry section 8.3, page 377.

Using natural rubber as a model, Staudinger conducted hydrogenation experiments and showed that hydrogenated rubber was very similar to normal unsaturated rubber. He provided experimental evidence that the molecular mass remained unchanged during the chemical modification.

Despite extensive experimental evidence, many leading chemists still opposed his ideas by suggesting that his products were impure. However, he continued his research on natural rubber and synthetic polymers, which were being synthesised by others trying to determine the molecular weights through various techniques including crystallisation.

Staudinger recognised and emphasised the significance of macromolecules in biochemistry and created a new research discipline of macromolecular bioscience. By the late 1930s, he had many supporters and the field of polymer science was firmly established with the concept of macromolecules being well researched and documented.

From ethylene to polymer

As you discovered in Activity 4.2, polyethylene (sometimes called polyethene or polythene) can be identified by two plastic identification codes – numbers 2 (high-density polyethylene, HDPE) and 4 (low-density polyethylene, LDPE) both of which are used for a wide variety of products.

Figure 4.7 ▶ Products made from polyethylene



Deb Smith

ACTIVITY 4.4

PROPERTIES AND USES OF POLYETHYLENE

Draw up a table to compare the properties and uses of low-density and high-density polyethylene using the information you obtained in Activities 4.1 and 4.2.

Polyethylene is produced by a **polymerisation** reaction in which ethylene molecules react together to form long chains. The ethylene molecules are called **monomers**.

The properties of LDPE and HDPE depend on the nature of the polymer chain. Highly ordered **crystalline** regions, which give strength to a polymer, form where molecules are uniformly arranged while **amorphous** (non-crystalline) regions form where the chains are randomly arranged and further apart.



To learn about how the monomer ethylene polymerises and the structural differences between LDPE and HDPE, refer to Chapter section 7.2, page 331.

You could model polyethylene by using spaghetti to simulate the packing of polymer chains.



To learn about how the degree of crystallinity affects a polymer, refer to Chemistry section 7.3, page 339.

WOW

The accidental discovery of polyethylene

In 1933, British scientists Reginald Gibson and Eric Fawcett were investigating high-pressure gas reactions at about 2000 atm as a way to make chemicals add together. One of the chemicals was ethylene. Discovering their apparatus leaked, they added more ethylene and left it to react over the weekend.

The following Monday when they opened the reaction vessel they found a waxy, white solid, which upon analysis had an empirical formula CH_2. They had a lot of difficulty trying to reproduce the reaction and abandoned the work.

Two years later, the work was restarted and they found a way to control the heat produced by the reaction, thus preventing an explosion. Michael Perrin took over the project and was able identify that the amount of oxygen needed was crucial for the new material, polyethylene, to form.

The leak in the original apparatus had allowed in just the right amount of oxygen, causing the ethylene to react to form polyethylene. Without this leak, polyethylene may never have been discovered.

ACTIVITY 4.5

POLYETHYLENE

Consider the data for low-density and high-density polyethylene in the following table. Use this information to answer the questions.

Polymer	Melting point (°C)	Density ($g\,mL^{-1}$)	Tensile strength (MPa)	% crystalline regions
LDPE	80	0.92	15	40–55
HDPE	135	0.96	29	70–80

a Will either of the polymers sink in water?

b Why does HDPE have more crystalline regions than LDPE?

c Why is the melting point of LDPE lower than that of HDPE?

d Why is the tensile strength of LDPE lower than that of HDPE?

e Use the information to explain why HDPE is an important material for hospital equipment while LDPE is used as a plastic food cling wrap.

To learn more about the reactions ethylene undergoes to produce these monomers, refer to Chemistry section 7.2, page 331.

Other addition polymers

Ethylene is used to produce polyethylene by **addition polymerisation**; about 60 per cent of all ethylene produced in Australia is used for this purpose. However, ethylene is also an important starting material for making other monomers, such as vinyl chloride, styrene, vinyl acetate and acrylonitrile, which are then polymerised by addition polymerisation to produce the important plastics – poly(vinyl chloride) (PVC), polystyrene, poly(vinyl acetate) (PVA) and acrylic.

Ethylene is also used to produce ethanol, which is used as an industrial solvent, a fuel and a reactant for making other chemicals.

To find out how these and other monomers with carbon–carbon double bonds polymerise, refer to Chemistry section 7.2, page 331.

The difference among polymers is the monomer used to form the polymer. When looking at the structures of ethylene, vinyl chloride, styrene and propylene, you should have noted that they all contain a carbon–carbon double bond, three hydrogen atoms and one variable atom or group attached to these two carbon atoms, $CH_2{=}CH{-}X$, where X is a hydrogen atom, chlorine atom or group of atoms. When monomers such as these, which contain a double bond, polymerise they do so by addition polymerisation. The monomers simply add to the growing polymer chain in such a way that the product contains all the atoms of the starting material.

The white foam cups that are used for hot drinks, and which are light, easily torn or broken and good insulators, are some of the most common examples of polystyrene. However, plastic cutlery, yoghurt containers and CD cases that are rigid and brittle are also made of polystyrene. Why are these items, which are made of the same polymer, so different?

The differences between polystyrene items are due to the way the polymer is manufactured, whereas the differences between low- and high-density polyethylene is in the amount of branching of the polymer chain.

POLYSTYRENE

Watch this video to see how polystyrene is turned into polystyrene foam.

The light foam form of polystyrene, sold under the trade name Styrofoam, is produced by blowing a gas through the polymerising liquid styrene until it froths up into a foam. As polymerisation occurs, the material solidifies and traps the gas within the solid, so producing the solid foam. The partially polymerised (partly solid) material can be moulded into various shapes (for example, cups) that become quite rigid as polymerisation goes to completion. Because it contains so many bubbles, it is not only light but is also an excellent insulator of heat. The hard plastic version of polystyrene is made without the introduction of a gas. The molten polymer can then be moulded into desired shapes; it solidifies into a clear brittle plastic.

A foam typically used in basketball shoes is an ethylene–vinyl acetate **copolymer** that has air whipped into it in a similar process to that used in producing Styrofoam.

ACTIVITY 4.6

STYROFOAM

Styrofoam is commonly used as a packaging material. The gas within the polymer absorbs the shock, like an airbag in a car, and so protects the packaged item. A typical piece of Styrofoam packaging such as the 'peanut' shaped ones used for mail parcels has a mass of 0.040 grams.

Calculate how many styrene monomer units are in one piece of Styrofoam packaging. (Remember, there are 6.02×10^{23} molecules per mole.)

To learn about how to calculate the yield of a chemical reaction, refer to Chemistry section 9.4, page 415.

Food packaging concerns

As was mentioned earlier, packaging accounts for over one-third of plastics. There is a huge variety of food packaging because it has to be designed to keep the food or drink safe, fresh and available. Other functions of food packaging include safeguarding, storing and dispensing the food.

Products containing fats and oils are especially sensitive to reaction with oxygen, which turns them rancid and causes them to taste and smell bad. Unsaturated fats, those with one or more carbon–carbon double bonds, are especially vulnerable.

Red meats are very sensitive to oxidation. Usually, they are wrapped in a plastic with low oxygen permeability and shipped in airtight containers. However, without exposure to oxygen, they turn a dull red, purplish colour due to **myoglobin**, a chemical related to haemoglobin, which transports oxygen in the blood.

This colour is not very appealing to consumers, so at the market the meats are rewrapped in a plastic that is **semipermeable**, which means it allows oxygen to enter while keeping water molecules from escaping. The plastic wrap chosen for rewrapping meats is either composed of LDPE or PVC.



Deb Smith

▲ **Figure 4.8**
Different types of food packaging

Upon contact with oxygen, myoglobin is converted to **oxymyoglobin**, which is bright red and makes the meat more appealing to the customer. However, upon further exposure to oxygen, the meat begins to deteriorate, turning brown and developing a poor taste and smell.

Fresh fruit and vegetables are quite different from meat because they benefit from exposure to oxygen, using it for respiration, which allows the natural ripening of the fruits even after they are picked. Most packaged fruits and vegetables will have many holes in their packaging to allow respiration to occur. An alternative is to wrap the fruit or vegetables in oxygen-permeable plastics, allowing respiration to still occur.

If fruit and vegetables are wrapped or stored in a plastic that does not have holes or does not allow oxygen to enter, then they will begin to break down and spoil.

Although plastics are designed to keep food fresh and safe, there are increasing public concerns that chemicals from food containers and wrapping might be leaching into food.

While the polymers themselves are too large to migrate into the food, the **plasticisers** and **stabilisers** added to the polymer are much smaller molecules and there are claims that they are being released and entering the food the wrap was designed to protect.

While research on the effects of additives to plastics used in food packaging is being undertaken, scientists are divided about their long-term effects.

Science can be limited in its ability to provide definitive answers to public debate; there may be insufficient reliable data available, or interpretation of the data may be open to question. (ACSCH086 and ACSCH124) AC

To learn how plasticisers affect the properties of a polymer, refer to Chemistry section 7.2, page 331.

ACTIVITY 4.7

HEALTH CONCERNS

Read the two articles in the weblinks and conduct your own research to put forward an argument as to whether the claims are valid on the basis of current available data.

ENVIRONMENTAL HEALTH PERSPECTIVES

Read the article about food packaging.

PLASTICS AND FOOD

Read the article about plastics and food.

Teflon – a non-stick polymer

The hydrophobic properties and unreactive nature of the material led to its use in the Apollo spacecraft to insulate electrical wires.



To learn about the addition reaction that produces PTFE, refer to Chemistry section 7.2, page 331.

Polytetrafluoroethylene (PTFE) is a polymer you are probably more familiar with as Teflon. It is most commonly known as the non-stick surface on pans, but it is also used to treat carpets and fabrics to make them stain resistant and has also been used for making artificial body parts. This polymer is also very strong. It is used to make high-grade electrical insulation and pipe thread sealant. The major application, using approximately 50 per cent of PTFE production, is insulation for wiring in aerospace and computer applications.

The discovery of Teflon, like that of polyethylene, was accidental. In the 1930s, scientists at DuPont laboratories were conducting research to find a non-toxic refrigerant. One chemist working on the project opened a new tank of tetrafluoroethylene gas and nothing came out. When he weighed it, the mass was the same as a full tank so he sawed it open and found a white powder. The gas had polymerised and formed the polymer PTFE.

This polymer has repeating units similar to those of polyethylene except all the hydrogen atoms have been replaced with fluorine. Its properties are due to the polar carbon–fluorine bonds and dipole–dipole interaction between polymer chains, which make it strong and tough. It also has the third lowest coefficient of friction of any solid and is resistant to the formation of dispersion forces, which means it is the only known surface geckos cannot stick to.

Figure 4.9 ▶
Non-stick frying pans are coated with pigmented Teflon; pure Teflon is white.



Zoonar GmbH/Alamy

ACTIVITY 4.8

HOW STRONG IS TEFLON?

Teflon tape is used by plumbers to make a waterproof seal between threaded iron pipes. You can buy Teflon tape at most hardware stores.

a Cut a 20 cm piece of tape, take a firm grip on each end and stretch it a bit lengthwise. What do you observe?

b Stretch the tape a little widthwise. What do you observe?

c Try to break the tape by stretching it slowly lengthwise. Use as much force as you need.

d Try to break the tape by stretching it widthwise. What do you observe?

e Use what you know about bonding to try to explain what you observed.

WOW

Gore-Tex

Teflon is used with other polymers to create a fabric that is water repellent and wear resistant. One fabric known for its water resistance is Gore-Tex.

Gore-Tex fabric is a waterproof material that consists of a Teflon film, a **hydrophobic** polymer, which is actually a membrane, attached to a conventional synthetic fibre such as nylon or polyester.

The pores in the Teflon membrane are about 20000 times smaller than a raindrop but 700 times larger than a molecule. This means the drop is too large to pass through the pore and the surface tension of the water keeps the molecules from passing through. However, water vapour from perspiration can pass through the pores from the inside out because it is only individual water molecules. This means the fabric can 'breathe', an important requirement for apparel, but is waterproof (compare with a PVC raincoat).

GORE-TEX

Visit this website for more information on Gore-Tex fabric.

Rubber – an interesting polymer

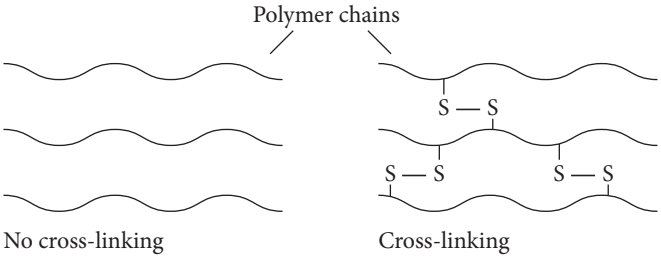
Natural rubber is an interesting addition polymer. It can be obtained from tree sap from many parts of the world, including Brazil, Sri Lanka and Malaysia. The rubber is obtained as **latex**, which is the sap of the tree. It is a **colloidal suspension** of nanoscale rubber particles in water.

Natural rubber is an addition polymer produced naturally by joining isoprene (2-methylbuta-1,3-diene) to make polyisoprene, which has structure shown in Figure 4.10.

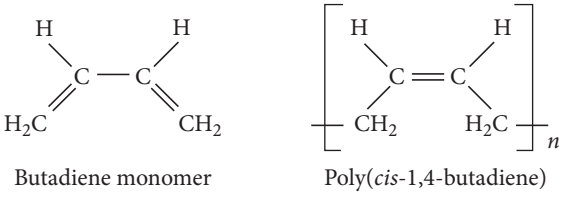
In natural rubber, the configuration across the double bond is 98 per cent *cis* (both CH_2 groups are on the same side of the double bond). This arrangement gives rise to rubber's property of increasing strength when stretched by allowing the chains to line up and form crystalline areas.

Unfortunately, natural rubber has many limitations because it is a **thermoplastic**. It cannot be used on its own to make tyres because in hot summers it would melt, whereas in cold winters it would become very hard and brittle.

In 1839, American inventor Charles Goodyear accidentally heated rubber and sulfur together and produced a new version of rubber that did not become sticky and melt at high temperatures. This process of reacting rubber with sulfur is called **vulcanisation**. The new rubber is a hard, durable material due to the cross-linking between polymer chains due to the sulfur atoms.

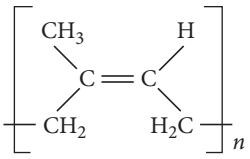


Attempts to synthesise natural rubber in the laboratory initially produced a product of poor quality because it was a mixture of *cis* and *trans* isomers. Chemists found they could produce a better quality rubber if they began with the monomer butadiene to produce poly(butadiene).



To learn more about how the properties of polymers are related to their structure, refer to Chemistry section 7.3, page 339.

To understand about the structures involved in rubber, you need to know about cis *and* trans *isomers. Refer to Chemistry section 6.2, page 286.*



▲ **Figure 4.10**
Polyisoprene

◀ **Figure 4.11**
Cross-linking in rubber

◀ **Figure 4.12**
Monomer of butadiene and the polymer it forms

To learn about copolymers, refer to Chemistry section 7.2, page 338.

However, the best synthetic rubber is actually a copolymer of butadiene and styrene, which produces styrene–butadiene rubber (SBR). The process used to produce SBR is called emulsion polymerisation, and it involves polymerising the butadiene and styrene in water using a **surfactant** to give a colloidal dispersion of the polymer in water.

There are many types of synthetic rubber available today that have much better properties than natural rubber. Today, about 80 per cent of the rubber produced is synthetic rubber.



Chris Howes/Wild Places Photography/Alamy

Figure 4.13 ▶ Car tyres are made from a mixture of natural rubber and synthetic rubber – a styrene–butadiene copolymer.

Revise what you learnt about intermolecular forces and the idea that 'like dissolves like' in Nelson Chemistry Units 1 & 2 for the Australian Curriculum, *Chapter 6.*

We have looked at polymers made from hydrocarbons; now we will consider a different group of polymers.

Thirsty polymers

You have already learnt about many polymers with different uses, but all these polymers have a structure that makes them insoluble in water. Sometimes we need a polymer that is either soluble in water or will absorb water.

In hospitals, there is the risk of infection from soiled laundry if it is improperly handled. This risk can be minimised by reducing the amount of handling. One way of doing this is to place the soiled laundry in plastic bags that will dissolve in the wash, thus removing the need to handle the items when transferring them from the hospital ward to the laundry to the washing machine. The bag of soiled linen is placed in the machine and during the wash the bag dissolves, releasing the items. Clean items are then removed from the machine so there has been minimal contact with the soiled linen.

Ethenol



Polyethenol

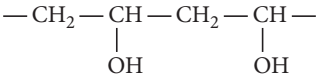


Figure 4.14 ▲ Polyethenol (polyvinyl alcohol), which is made from the monomer ethenol (vinyl alcohol), is a dissolving plastic.

The dissolving plastic must be composed of chemical groups that are capable of dipole–dipole interaction or hydrogen bonding so it will dissolve in water. One dissolving plastic is polyethenol, also called poly(vinyl alcohol), which has many OH groups that can hydrogen bond to water so the polymer dissolves.

Polymers that dissolve in water are very useful, but it is also useful to have polymers that absorb water and other liquids but don't dissolve.

Water-absorbing polymers are called hydrogels. Some familiar examples of hydrogels are contact lenses, absorbent material in disposable nappies, water-absorbing crystals and hair gel.

A variety of polymers are used to make hydrogels, but they are all cross-linked networks swollen with water. To absorb water, they must be **hydrophilic**, which means they must contain chemical groups capable of forming hydrogen bonds with water. These chemical groups usually contain an O–H or N–H bond.

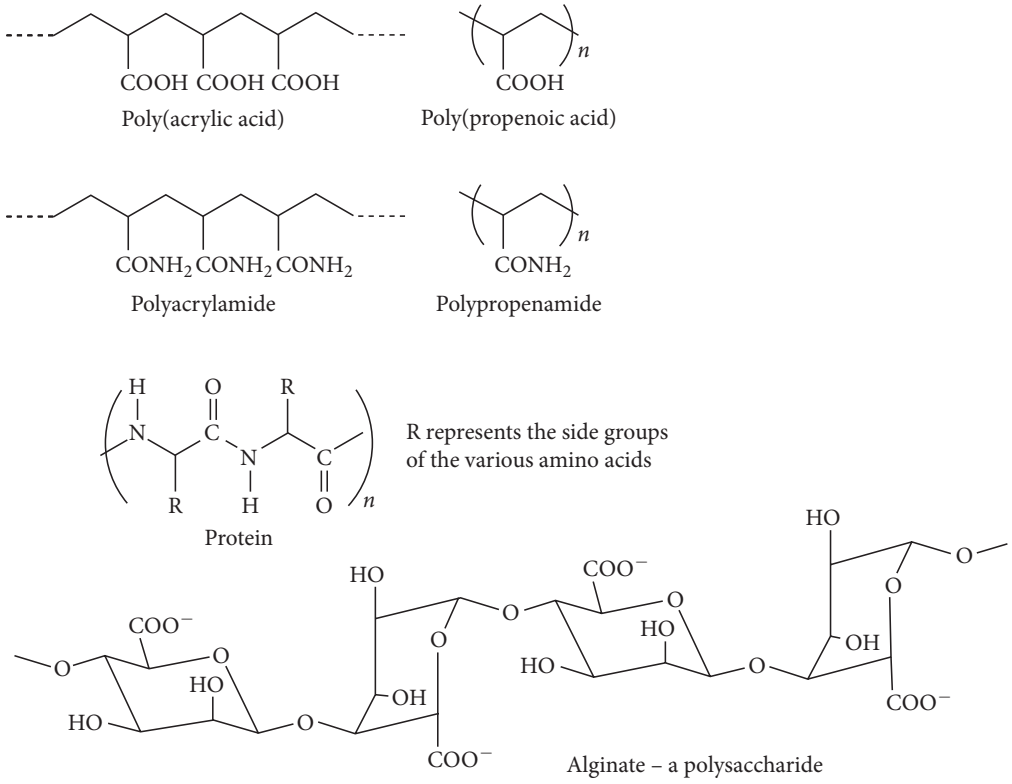
Examples of hydrogels are synthetic polymers, such as polyethenol, poly(acrylic acid), poly(acrylamide) and naturally occurring polymers based on proteins (e.g. gelatine) and carbohydrates.

To learn about functional groups and alcohols, refer to Chemistry sections 6.5 and 6.6, pages 296 and 298.



Deb Smith

◀ **Figure 4.15**
Some common hydrogels – jelly, water-absorbing crystals, hair gel and disposable nappies



◀ **Figure 4.16**
Structures of some polymers used to make hydrogels

In order to be effective as hydrogels, these polymers must be cross-linked – joined together to form a network. This means the hydrogel is essentially one enormous molecule. If the cross-links did not exist, then the polymer would simply dissolve in water, like the polyethenol plastic bags, rather than forming a gel, so contact lenses would be dissolved by tears, jelly would never set and disposable nappies would be totally useless.

The cross-links may be different types as long as they hold the molecule together when it is placed in water. In many cases, the cross-links are covalent bonds, as in contact lenses or super absorbers, or they may be ionic linkages as in hair gel or they can be actual physical entanglements such as those that hold gelatine together.

Figure 4.17 ▶
Schematic picture of a cross-linked hydrogel

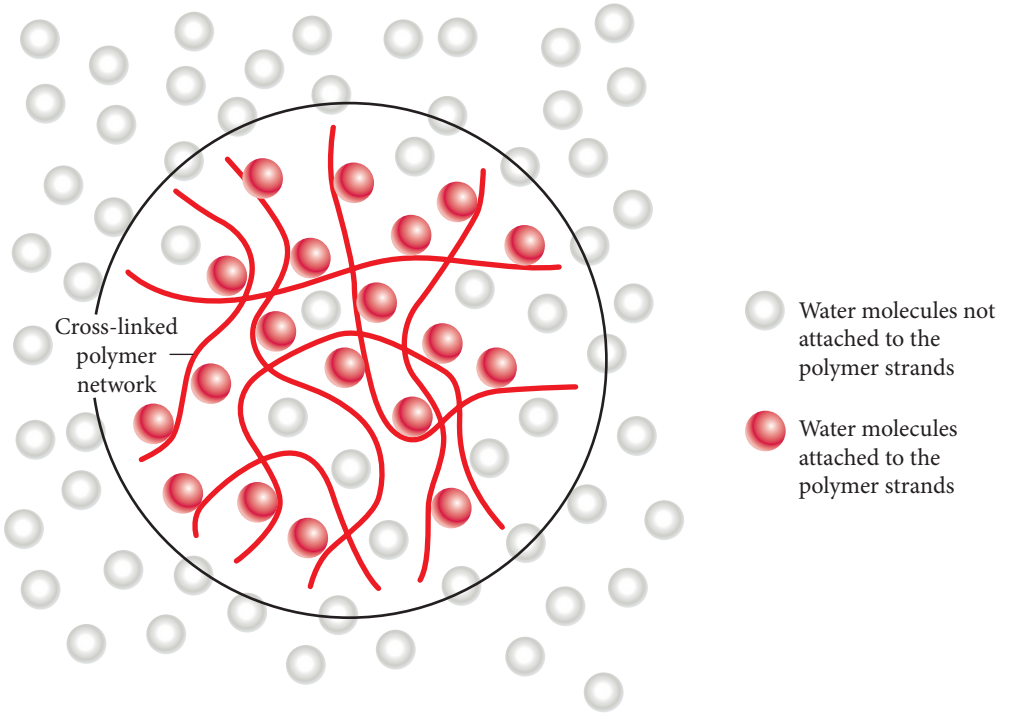
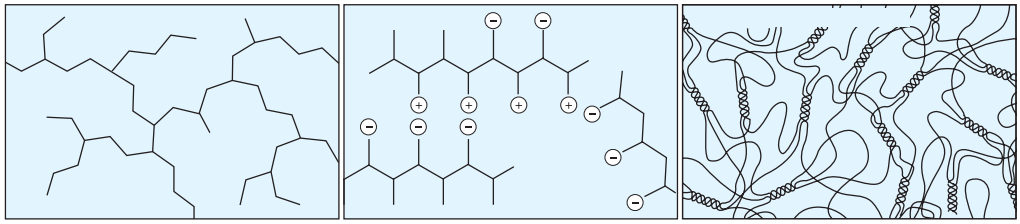


Figure 4.18 ▶
Various types of cross-links



Contact lenses were originally made from poly(methyl methacrylate), PMMA, which is the same polymer from which Perspex is made. PMMA was well suited to be used in contact lenses since it was transparent, tough and scratch resistant. However, the lenses were quite rigid, which made them uncomfortable to wear and they also prevented oxygen reaching the eye. Hence, they had to be taken out regularly to allow oxygen to reach the eye. Now, contact lenses are made from hydrogels such as poly(hydroxyethyl methacrylate), polyHEMA. This material is approximately 40 per cent water, so it is much softer and more comfortable to wear. It also allows oxygen through to the eye; these lenses do not need to be taken out as often as those made from PMMA.

There is quite a bit of interest in the potential medical applications of hydrogels such as implantable devices such as cartilage replacement, breast implants, wound dressings and drug delivery devices because the body does not easily recognise them as foreign materials so they are not rejected.

ACTIVITY 4.9

HYDROGEL

a Draw a diagram to show how water is bonded to a hydrogel with ionic cross-links.

b Cover a blob of hair gel with salt and describe what happens. Explain your observations.

WOW

Using hydrogels to block fires

The chance discovery of an unburnt nappy among the charred remains of a fire led to the development of a hydrogel protection system for any surface exposed to fire. When a gel coating is spread over the surface of materials, it acts as a barrier to the spread of fire. The bound water in the hydrogel has a higher boiling point due to the strong intermolecular forces between the water and the gel. The hydrogel also holds a large amount of water, which naturally has a high heat capacity and high heat of vaporisation, so a lot of energy can be absorbed by the bound water.

Marketed as Barricade®, the hydrogel pumped full of water can be sprayed on the material to be protected and then washed off with water when the danger has passed. The gel effectively retards the flames, also giving a high level of protection from radiant heat and embers.

HYDROGEL

Visit this website to find out about a new hydrogel based on DNA.

CHEMISTRY BREAKTHROUGH

Visit this website and read the story of how international collaboration between scientists led to an amazing breakthrough in polymer chemistry.

International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region. (ACSCH087 and ACSCH125) AC

To understand this section you need to know about alkynes, and delocalised electrons. To learn about alkynes and delocalised electrons, refer to Chemistry sections 6.2 and 6.4, pages 288 and 295.

Conducting polymers

Polymeric materials have excellent electrical insulating properties and are practically indispensable for that purpose. The first synthetic polymer, Bakelite, is still used to make light fittings and electrical sockets though not the faceplates. We could not sustain our complex electrical and electronic technology without the use of excellent insulating materials that are also tough, flexible, light in weight and easily fabricated in a wide variety of shapes.

However, there are problems with using conventional insulating plastics. When used to make the outer cases of electronic communication equipment (e.g. telephones and radios), they allow radio waves to pass unhindered to the internal circuitry, causing electronic pollution. Another problem arises from the build-up of static electricity, which leads to sparking and interference. Sparking also presents a potential threat for serious fire or explosion if flammable substances are present. One way to overcome these problems is to have some conductive material in the outer cases.

Conductive polymer **composites** made up of two or more different materials, in many instances a metal or graphite plus a conventional insulating polymer, can replace conventional insulating plastics so avoiding the problems of electronic pollution and static.

In 2000, Hideki Shirikawa, Alan MacDiarmid and Alam Heeger were jointly awarded the Nobel Prize in Chemistry for the discovery of polymers that conduct like metals, by the movement of electrons along and between the polymer chain. The story of the discovery of the first conducting polymer is one that involved three different scientists from three different disciplines working together.

The archetypal conducting polymer is polyethyne, which is produced by the polymerisation of ethyne (HC≡CH). This polymer has alternating single and double bonds:

—CH=CH—CH=CH—CH=CH—

There are two forms of the polymer because geometric isomerism means that there are two ways the double bonds can be arranged relative to one another. Of course, polymer chains containing mixed arrangements are also possible.

ACTIVITY 4.10

POLYMER CHAINS

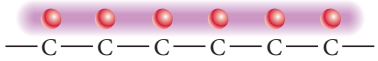
a Draw a diagram to show a section of the ethyne polymer chain with the *cis* arrangement.

b Draw a section of the chain showing the *trans* arrangements.

Molecules with alternating single and double bonds are called **conjugated** systems. As in benzene, some of the electrons are not localised between particular pairs of carbon atoms but are spread out over all the carbon atoms. In benzene, six electrons are spread out above and

below the ring of the carbon atoms in a delocalised cloud. Similarly, in polyethyne there is a delocalised cloud spread out along the carbon chain; each C atom contributes one electron to this cloud:

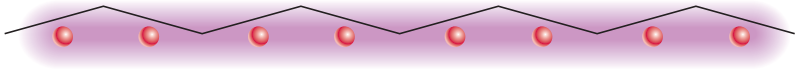
Figure 4.19 ▶ Polyethyne showing a delocalised electron cloud



The result is that all the bonds are identical – intermediate between single and double – and the electrons are able to move fairly readily under the influence of an electric field.

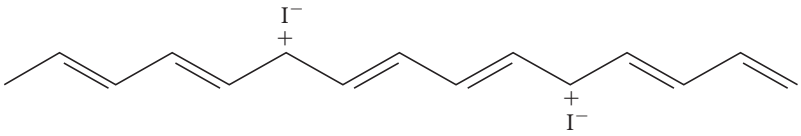
The *trans* isomer, which is a better conductor than the *cis* isomer, is shown in Figure 4.20.

Figure 4.20 ▶ The *trans* isomer of polyethyne, showing delocalised electron cloud



While polyethyne has an electrical conductivity much greater than the common synthetic polymers, it is still not high enough for practical use. In addition, polyethyne is somewhat unstable in air. The problem of low conductivity was solved by doping the polymer with iodine, which is an electron acceptor ($I_2 + 2e^- \rightarrow 2I^-$). When iodine accepts an electron, a positively charged carbon atom is formed in the polymer at points where the sequence of double and single bonds reverse, as shown in Figure 4.21. The positive charges move easily along the chain from carbon to carbon, creating a backbone that is very conductive.

Figure 4.21 ▶ Doping with iodine produces positive C atoms along the polyethyne chain



The iodine-doped polymer conducts electricity 1 000 000 000 (one billion) times better than previous forms. The instability of this polymer in air is still a problem to be solved.

Many other conjugated conducting polymers have been developed in recent years and although these do not have the high degree of conductivity evident in polyethyne, they are much more stable.

A chance discovery occurred when one of these conjugated polymers had a voltage applied across it. It glowed with an eerie green light. This has led to the further development of new polymers that emit light when a voltage is applied.

Philips, Osram and Toshiba commercialised the technology in mobile phones and portable digital assistant (PDA) screens in 2002 and the field of conducting polymers took off. There is still enormous potential for these polymers to be used as video and computer screens 2 mm thick, and television screens that can be rolled up when not in use.

Clothes from plastic bottles



To understand how polyesters are made, you need to understand about carboxylic acids and esters. To learn about these classes of compounds, refer to Chemistry sections 6.8 and 6.9, pages 307 and 310.

It might seem strange that plastic soft-drink bottles and T-shirts are made out of the same thing – but they are. They are both made out of the polymer polyethylene terephthalate, or PET. When this polymer is made into fibres for textiles, it is generally called **polyester**.

Although the term 'polyester' is commonly used when referring to PET fibres, it is not the only type of polyester polymer. First let us examine PET and then we will look at other polyester polymers and their uses.

PET is a thermoplastic, which means it can be repeatedly melted and reshaped. When heated, molten PET can be pressed into moulds to make bottles or furniture, or it can be spun – squeezed through tiny holes to form fibres that can be woven into fabric for use in carpets, clothing or quilts. In the fibre form where it is used to make clothes, it is commonly known by the trade names Terylene® and Dacron®.



Deb Smith

◀ **Figure 4.22**
The same polyester is used to make both soft-drink bottles and clothing.

When the product reaches the end of its useful life, PET can be recycled. It is a recycling success story. This polymer has the plastics identification code number 1 and is used for making a huge variety of recycled products, including clothing, carpet, luggage, bottles, tote bags and food and beverage containers.

Five 2-litre bottles can be transformed into one T-shirt or the fibrefill insulation for one ski jacket. One square metre of polyester carpet can be made from 36 bottles.

PET is also known as polyester and as the name suggests it is formed by the same type of reaction (esterification) that produces esters – a reaction between an alcohol and a carboxylic acid.

PET is a copolymer because it is made from two different monomers – one containing the –OH group and the other containing the carboxylic acid group –COOH. In order to make this polyester, the alcohol must have two –OH groups and the acid must have two –COOH groups so the polymer chain can grow. Unlike the polymers already studied, PET is not formed by an addition reaction. It is produced by a condensation reaction and so is classified as a **condensation polymer**. Natural polymers formed this way include cellulose, starch, wool, silk and proteins.



To learn about condensation reactions and how polyester is formed, refer to Chemistry section 7.4, page 343.

Hydrolysis of polyesters

Polyesters are readily attacked by alkalis but more slowly by dilute acids. They undergo hydrolysis reactions similar to esters. Hydrolysis by water alone is so slow as to be unimportant.

If a dilute alkali such as NaOH is spilt on a fabric made from polyester, the ester linkages are broken. The original alcohol, ethane-1,2-diol, is formed together with the sodium salt of the carboxylic acid.

The fibres of the fabric are destroyed and a hole forms in the fabric.

On page 92, we discussed some alcohol-based polymers that dissolve in water. We will now consider a different reason for wanting polymers that dissolve and the compounds that have been developed for this purpose.



To learn about hydrolysis of esters, refer to Chemistry section 6.9, page 312.

Polyesters that dissolve

Another use for polyester polymers in the medical field is as sutures that are used to stitch together the sides of wounds, mending and growing bone tissue, controlled drug release and tissue engineering.

The earliest known suture, around CE 150, is believed to have been catgut, which was used by a Greek physician to stitch together wounded gladiators. Today's surgeons use a synthetic biodegradable polymer created to be biocompatible, and which has good tensile strength and dissolves in the body by natural action.

To learn about how the arrangement of side groups affects polymer properties, refer to Chemistry section 7.3, page 339.

To learn how these techniques work, refer to Chemistry sections 8.2 and 8.4, pages 369 and 384.

One common biodegradable polymer is a polyester made from just one monomer that contains an alcohol group on one end and a carboxylic acid group on the other (unlike PET, which is made from two different monomers). The threads are strong but the water in the body causes them to slowly hydrolyse back to the original monomer units.

The polyester thread is made by polymerising lactic acid (HO—$CHCH_3$—COOH) or glycolic acid (HO—CH_2—COOH) through an esterification reaction. The products that result from the breakdown (hydrolysis) of these polymers are non-toxic; in fact, lactic acid is formed naturally in the body as a product of the breakdown of glucose.

Lactic acid is an asymmetrical molecule so the relative positions of the alkyl, carboxyl and alcohol groups influence the properties of the resultant polymer. It may be hard, crystalline and durable or rubbery and durable. As you have already learnt, molecular mass will also affect the polymer's properties.

To ensure the quality of the end product, molecular mass and stereochemistry of the polymer must be quality assured. This is done by using chromatography, mass spectroscopy and nuclear magnetic resonance (NMR) spectroscopy.

Each polymer has particular advantages, so copolymers of both glycolic acid and lactic acid are also commonly used as biodegradable sutures to balance the greater strength of poly(glycolic acid) with the slower degradation of poly(lactic acid).

Biodegradable polyesters are also used to control the rate of delivery of a medicine into the body. The chemical packing that encloses the medicines is specifically formulated to provide precise, controlled and sustained doses.

Some oral medicines can be designed to be gradually released into the body over a specified time interval by carefully designing the coating that encapsulates the medicine. For example, the decongestant Contac® contains tiny beads of medicine that are covered with a water-soluble polymer coating of various thicknesses. The thicker the coating, the longer it takes to dissolve and the slower the medicine is released. This coating is quite separate from the gelatine capsule that contains all the beads; the capsule itself dissolves relatively quickly.

'Twelve hour medicines', those that claim to be effective for that period of time, contain a mixture of beads of medicine coated in a variety of thicknesses of polymer. Thin, coated beads are dissolved quickly while those with a thicker coat will take up to 12 hours to dissolve.

Some oral medicines are chemically formulated to achieve delivery in a specific part of the digestive system. The coating can also be designed to respond to the acidity of its environment. The contrasting acidity of the stomach and basic environment of the intestines means a coating that is stable in an acidic environment but dissolves in a basic environment can ensure the drug is released at the required place in the digestive system. For example, aspirin caplets are coated with a polymer of ethyl cellulose, which allows them to pass through the stomach to the intestine before they dissolve. This also helps prevent stomach irritation.

Transdermal patches, such as those used by people trying to give up smoking or as a contraceptive, have a polymer coating that is responsive to temperature or moisture.

The sophistication of the technology of time-release medications arises from the extensive structural control chemists have over the design of different polymer coatings.

TRANSDERMAL PATCHES

Visit this website to find out more about transdermal patches.

ACTIVITY 4.11

TIME-RELEASE ASPIRIN

Design and perform an experiment to see how various conditions such as pH and temperature affect the solubility of different aspirin caplets.

Nylon – a polyamide imitating nature

Nylon is one of the first and most successful synthetic fabrics. The first nylon was created as a replacement for silk, which was expensive and difficult to obtain. Today nylon is used in making everything from tents to fishing lines; from parachutes to machine parts. Nylon carpeting lasts longer and is more economical than other natural and synthetic fibres. Compared with natural fibres it is stronger, lighter and more water resistant.



This Way to Nylon Stocking Sale, Hagley Digital Images, HF_N070_124, Hagley Museum and Library

◀ **Figure 4.23**
Crowds of women lined up to buy stockings when they were first released in 1940.

To understand the chemistry involved in producing nylon, you first need to know about two nitrogen-containing organic groups – amines and amides. Refer to Chemistry section 6.10, page 316.

Nylon's first real success came with its use in women's stockings. On 15 May 1940, nylon stockings ('nylons') first went on sale to the public in New York and within a few hours 4 million pairs had been sold. However, the first nylon product to appear on the market was actually a toothbrush with nylon bristles.

The entry of the United States into World War II saw the development of nylon's use to make war materials such as parachutes and ropes. This meant that nylon stockings were not generally available until the end of the war.

Nylon belongs to the group of polymers called **polyamides** because of the characteristic amide linkage in the backbone of the polymer chain. Polyamides are one of the most important classes of natural polymers, proteins.

Although we generally refer to nylon, there are actually many different types of nylon depending on the monomer or monomers used to make it. A nylon is made by a **condensation polymerisation** reaction between an amine ($-NH_2$) group and a carboxylic acid ($-COOH$) group.

The molecular mass of nylon is crucial. It should be between 12 000 and 20 000 if the fibre is to be strong. The growth of the polymer molecule can be stopped at a particular point if one reagent is limiting. It was found that if a ratio of 1 diamine to 1.02 diacid is used, a polymer with a molecular weight of 12 000 is produced, which is suitable for the production of the fibres.

The fibres are made by extruding molten nylon through tiny holes to form filaments (thin strands), which are cooled and wound onto large bobbins. When the filaments are first produced, they are dull and not very strong. To increase their strength, the filaments are stretched, increasing their length by 17 per cent. The stretching causes the randomly oriented molecules to align in the direction they are stretched.

Although nylon fibres are extremely strong, waterproof and durable, nylon fabric lost its popularity because it did not 'breathe'. Its hydrophobic nature meant that the fabric would not

To learn about the polymerisation reactions that form nylon, refer to Chemistry section 7.4, page 343.

absorb moisture nor would it allow water vapour to escape through its weave. This meant that on hot days, perspiration could not escape and the wearer became sweaty and uncomfortable.

This problem was solved by changing the texture and shape of the yarn. By blowing air at high pressure through bundles of filaments, loops were created along the filament. Then when the fibre is woven, the loops give the fabric a texture and feel similar to cotton. The loops allow water vapour to escape the fabric but don't allow the larger water molecule to enter, thus creating a fabric that can 'breathe' but which is still non-absorbent.

ACTIVITY 4.12

NYLON VS POLYESTER

Obtain pieces of nylon and polyester fabric. Design an experiment to compare the properties of each. You could look at properties such as water absorbency, breathability, strength, durability, stretch and resistance to acids and bases.

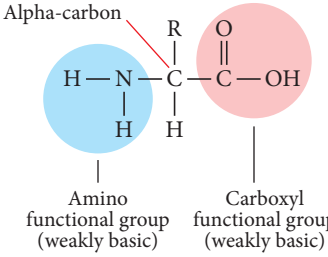


Figure 4.24 ▶ An alpha-amino acid. R = H or organic group (there are 20 possibilities for R for the amino acids commonly found in proteins)

To learn more about these biological polymers, refer to Chemistry section 7.6, page 354.

PROTEINS

Visit this website to find out about freely available software that allows scientists to visualise the structure of proteins.

ICT and other technologies have dramatically increased the size, accuracy and geographic and temporal scope of data sets with which scientists work. (ACSCH082 and ACSCH120)

Proteins are polyamides too

All proteins, including those that make up our skin, hair, muscle and enzymes, are also polyamides. They are condensation polymers of amino acids. Amino acids are compounds with a $-COOH$ at one end and a $-NH_2$ group at the other. They have the general formula shown in Figure 4.24.

The 20 amino acids found in proteins differ in the identity of their R groups. When proteins form, different amino acids are strung together sequentially in the one chain.

Given that there are 20 naturally occurring amino acid building blocks, the variety of proteins that can be synthesised is enormous. The properties of the protein depend as much on the sequence of amino acids as upon the number of them in the chain. Some proteins are made up of only a few amino acids while others are made up of hundreds.

Proteins have much more complicated structures than synthetic polymers, and developments in computer modelling have enabled more accurate visualisation and prediction of three-dimensional organic structures.

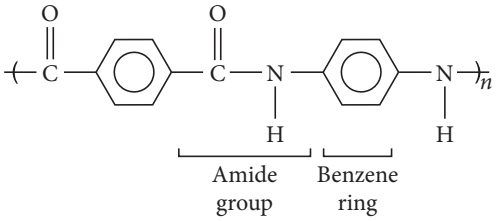
So far you have looked at two synthetic polymers that are commonly used to make fabric. Now let's consider a polyamide fabric that has quite different properties.

Kevlar® – fabric of steel

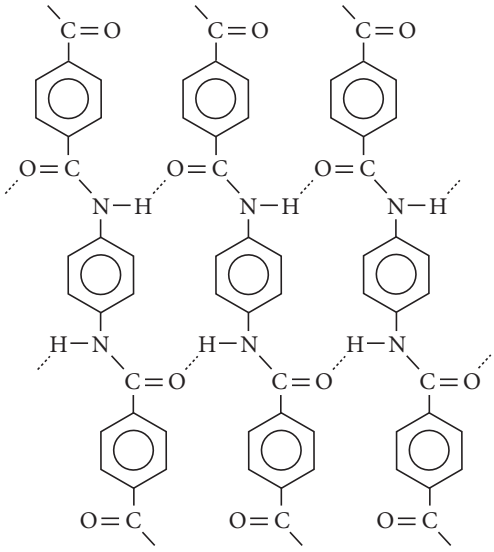
Following the development of nylon, chemists began to develop a better understanding of the relationship between the properties and structure of polymers. They were better able to predict the strengths and weaknesses of different structures, so in the early 1960s when looking for a polymer that was strong and heat resistant they realised putting an aromatic (benzene) ring in the polymer structure was likely to provide a good starting point. After trial and error, Kevlar was developed.

Five times stronger than steel, Kevlar has been used to make bulletproof vests and helmets for police and military forces. Its combination of strength and light weight means it has been used to make bodies of aircraft and spacecraft. Kevlar has been widely used in transmissions, cooling systems and brakes because of its ability to withstand high heat and abrasion.

Kevlar is a polyamide made from a diamine and dicarboxylic acid such as nylon-6,6 but with one major difference – it has a benzene ring instead of a straight chain between the amine groups in the diamine and between the acid groups in the dicarboxylic acid. It forms a polymeric aromatic amide – an **aramid.**



▲Figure 4.25
Structure of Kevlar



▲ Figure 4.26
Hydrogen bonding (dotted lines) between polymer chains

The strength of Kevlar comes from the combination of the amide and aromatic groups. The bulky, rigid aromatic rings keep the polymer chain straight and stiff. The amide group holds the polymer chains together by hydrogen bonds between adjacent polymers.

Another factor that contributes to Kevlar's strength is way the rigid, linear chains are packed together. The benzene rings can stack on top of one another like pancakes on a plate, forming sheets of molecules. The molecules line up in perfect array.

Making Kevlar fibres proved to be a challenge. Because the chains line up so precisely and bond together so strongly, almost no solvent will dissolve them. Kevlar is stable at high temperatures and cannot be melted. It will disintegrate before reaching its melting point. A chemist at DuPont found that the only suitable solvent was concentrated sulfuric acid and the company invested $400 million to construct a manufacturing plant.

Kevlar has many uses apart from those already mentioned. Ropes made from Kevlar have 20 times the strength of steel ropes of the same weight. Kevlar is also used in sporting equipment, protective gloves, fibre-optic cables and boats.

ACTIVITY 4.13

KEVLAR

Kevlar dissolves in concentrated sulfuric acid. Suggest why this occurs. (Hint: Look at the monomer structures and recall that acids are proton donors.)

WOW

Engineered spider silk

One of the most thoroughly studied and strongest known fibres is dragline silk, which is made by the golden orb-weaver spider. Spider's silk is an amazing material, which scientists are trying to produce synthetically. The silk is strong enough to bear the weight of a bungee-jumping spider (it can extend to almost three times its original length without breaking), flexible enough to withstand the impact of a flying insect, stable enough to last for days and insoluble in water.

Spider silk is stronger than any other known natural or synthetic fibre. It is as much as four times stronger than steel of the same diameter.

Proposals for possible uses of spider silk include wear-resistant fabric for clothing, super-strong reinforcing cables for bridges or catapult cables on aircraft carriers, bulletproof vests and artificial tendons and ligaments.

SPIDER SILK

Watch this video about how spider silk is being engineered.

There are many more polymers than the ones studied here so far and new polymers are continually being developed for many purposes. For example, there are polymers to replace bone, others that self-heal, and others for making shatterproof windows.

Green polymers



Michal Rosenstein

Figure 4.27 ▼ Polymers can be made using cellulose from plants

POLYMERS

Visit this website to find out more about almost anything to do with polymers. It shows how common polymers are in daily life and provides comprehensive details of the chemistry of most polymers.

To understand the design of synthetic processes and how to determine yield, refer to Chemistry sections 9.3 and 9.4, pages 409 and 412.

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126)

To find out more about biofuels, refer to Chemistry section 9.6, page 421.

To learn about the structure and polymerisation of cellulose, refer to Chemistry section 7.5, page 349.

Most synthetic polymers are made from raw materials derived from crude oil, which is a non-renewable resource. The world's oil reserves are being depleted, with analysts predicting that supplies will be effectively used up by the middle or end of this century. The other major problem is plastic pollution due to poor recycling habits of developed countries and the throwaway nature of the plastic products, including electronics and appliances.

The major use of crude oil is as fuel. Scientists are looking at possible alternatives given the concern of diminishing supplies and rising costs. Similarly, some scientists argue that we should be developing alternative sources of raw materials for plastics. They point to ethanol, already being used as a fuel supplement or alternative, as being a source of ethylene, a major monomer itself and the starting point for making many other monomers for common polymers.

Others argue that as oil supplies diminish, costs will increase and oil will become too expensive as a fuel. The plastic industry will be less affected by the price rises (because the cost of the raw materials is a smaller proportion of the cost of the finished product) and so will still be able to use oil. Consequently, these people argue, the remaining oil will become the exclusive domain of the plastic industry and will last for many more decades.

Regardless of which argument is correct, it would be prudent for the plastic industry to develop alternative sources of its core monomers – ethylene and propene.

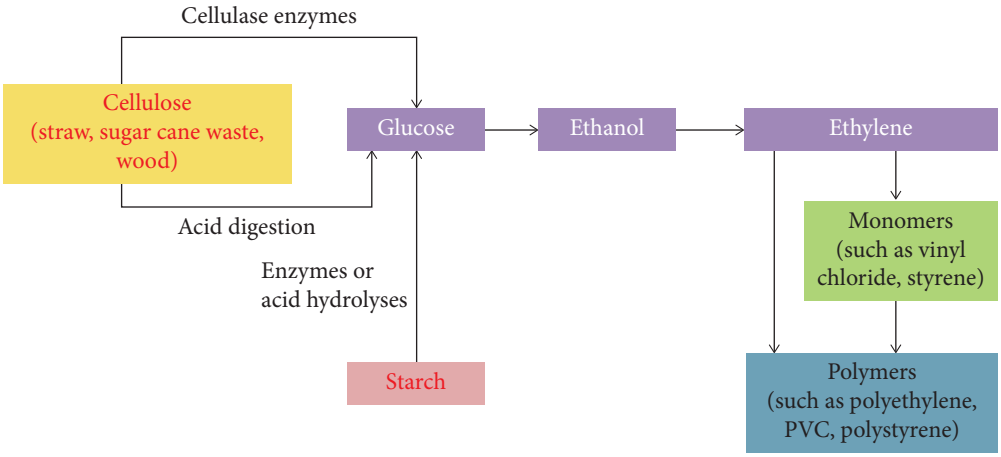
Ethanol is the prime candidate for such an alternative source of ethylene. Ethanol can be produced by fermentation of starches and sugars. These may be derived from a variety of agricultural crops, not just grapes, and the ethanol can be easily converted to ethylene.

However, another starting material increasingly being used for making many of today's polymers is cellulose. Cellulose is a major component of plant material, comprising up to 33 per cent of all vegetable matter, whereas starch and sugars are only minor components. It is a naturally occurring condensation polymer – a polysaccharide made up of 3000 or more monomer units of glucose.

Cellulose as a source of chemicals

Cellulose is widely used as cotton, particularly for textiles, and as paper and cardboard. But can it be used as a source of chemicals?

Each glucose unit of cellulose has six carbon atoms joined together (see Figure C7.23 on page 353), so it could be regarded as a basic structure for starting molecules for petrochemicals – molecules such as ethylene (2 C atoms), propylene (3 C atoms) and butane (4 C atoms, a starting point for synthetic rubber)



◀**Figure 4.28** Converting cellulose and/or starch to ethylene and various polymers



To learn about green chemistry using renewable raw material, refer to Chemistry section 9.7, page 424.



BIOPLASTIC

Watch this video, which shows the production of a bioplastic using corn.

The flowchart in Figure 4.28 shows how cellulose could be converted to ethylene, which could be used to make many of the polymers synthesised from ethylene derived from oil.

Unfortunately, it is very difficult to break cellulose into glucose. This is because the long near-linear chains of cellulose hydrogen bond to one another to form very compact fibres, making it hard for chemicals to access the glucose–glucose links. However, there are two processes for breaking cellulose into glucose:

1 *Digestion by cellulose enzymes*. These enzymes exist in bacteria present in the stomach of herbivores and in certain fungi. The process can be performed industrially by first treating the finely ground cellulose-containing materials (such as grain husks and stalks, bagasse and old newspapers) with sodium hydroxide solution (or sometimes just hot water) to swell (open up) the cellulose fibres, then digesting them with cellulose enzymes to produce a solution of glucose.
2 *Digestion with strong acid*. This involves heating a suspension of cellulose-containing materials (those mentioned above plus wood chips) with moderately concentrated aqueous sulfuric acid solution, which breaks cellulose into glucose. Insoluble matter, particularly lignin from wood pulp, is filtered off, many impurities are removed, and then the acid is neutralised to produce a solution of glucose.

In both cases, the solution of glucose can be treated with yeast to form ethanol, which can be dehydrated to ethylene if necessary.

While this conversion of cellulose to ethanol and then ethylene does work, much of the energy required for the process (keeping reaction mixtures hot and driving the process machinery) can originate from oil, so more oil would be used making ethylene this way than is used by cracking the oil directly to ethylene. Making ethanol from cellulose is considerably more expensive than making it from starch or sugars, despite the lower cost of the starting cellulose-containing material. Nevertheless, considerable scientific effort is being directed into developing more efficient ways of using cellulose as an alternative source of chemicals we now obtain from oil.

There is also the potential for algae grown in controlled large-scale environments to produce oils that can be converted to hydrocarbons and ethanol and hence be used as the raw materials for polymers. The advantage of algae, compared to plant crops, is that they grow very quickly and can be harvested within a week.

As well as using alternative starting materials for polymers, industry can reduce the amount of raw material needed to produce polymers by recycling.

Biopolymers – biopolymers from nature

Biopolymers are polymers that are made totally or in large part by living organisms.

Originally the word referred to biologically synthesised polymers such as cellulose, starch, proteins and nucleic acids. However, now it includes polymers that are chemically modified versions of natural polymers and polymers that can be produced by 'manipulating' biological organisms.

Partially synthetic biopolymers based on cellulose have been used commercially for nearly a century. The first plastic was cellulose nitrate, patented in 1869 as celluloid; it was a synthetically modified cellulose.

Some examples of renewable polymers and what they can be made from are shown in Table 4.1.

Table 4.1 Renewable polymers

Polymer	Crop or renewable material	Common uses
Starch-based polymers	Wheat, potatoes, corn	Compost bags, foam packaging fill, some food packaging
Polylactic acid (PLA)	Wheat, potatoes, corn	Food packaging, medical applications
Cellulose	Farmed wood	Cereal bar wrappers
Polyhydroxyalkanoates (PHA)	Plant derived sugars and oils	Medical devices such as orthopaedic pins
Polyesters	Corn	Textiles
Polyurethane	Soy or castor oil	Car seats
Polyethylene	Sugarcane	Resins

ACTIVITY 4.14

CORNSTARCH VS POLYSTYRENE PACKAGING

Aim

To determine whether cornstarch packaging is as effective as polystyrene packaging

What to do

Obtain some of each of the two types of packaging material – cornstarch pellets and polystyrene pellets. Design an investigation to test the effectiveness of the two different materials.

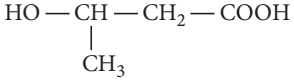


Figure 4.29 ▲ 3-Hydroxybutanoic acid is used to make the biopolymer poly (3-hydroxybutanoate) (PHA), which is biodegradable.

Another example is the biopolymer poly(3-hydroxyalkanoate) (PHA). This polymer has similar properties to the synthetic polymer polypropylene, but is biodegradable.

The simplest PHA is poly(3-hydroxybutanoate), or PHB. The monomer is 3-hydroxybutanoic acid, sometimes called β-hydroxybutanoic acid, and is shown in Figure 4.29.

The polymer is a polyester (same chemical linkage as PET). Although PHB has a different chemical structure from polypropylene, its physical and mechanical properties are quite similar.

To produce PHB, a culture of a micro-organism such as *Alcaligenes eutrophus* is placed in a suitable medium and fed nutrients so that it multiplies rapidly and grows into a large quantity. Then the 'diet' is changed to restrict the supply of one particular nutrient (such as nitrogen). Under these conditions, the organism is no longer able to increase its population but instead begins to make the desired polymer, which it stores for later use as an energy source. The amount of PHB that the organism can produce is 30–80 per cent of its own dry weight. The organism is then harvested and the polymer separated out.

PHB is much more expensive to make than oil-based polymers with similar properties. However, there is a growing demand for it where biodegradability is a prime consideration. Such applications include disposable nappies and packaging in the form of bottles, bags and wrapping film, particularly for medical and hospital supplies.

Much research is being conducted into biopolymers and some interesting polymers are being designed.

Food scientist Sirinivasan Damodaran, from the University of Wisconsin in the United States, has developed a super-absorbent material made from discarded fish parts. It is cheap and biodegradable so makes a perfect fill for disposable nappies.

By attaching water-binding molecules to protein extracts from waste fish, Damodaran has created a hydrogel that can absorb up to 600 times its own weight in liquid. This new hydrogel uses one type of rubbish (fish waste) to solve another rubbish problem (disposable nappies). Other potential applications of this hydrogel include as a moisturising agent in cosmetics and as an industrial decontaminant because it also binds to heavy metals.

Another potentially valuable source for the production of polymers is chitin, the second most abundant biopolymer on Earth after cellulose. It is the structural polymer that makes up the exoskeleton of crustaceans such as prawns, lobsters and crabs. Chitin can be converted very easily to the biopolymer chitosan.

There have been a number of uses of chitosan – it is used in shampoos and other hair-care products since it forms a clear, elastic film on hair so it feels smoother as well as increasing the mechanical strength of hair. It is also used in the treatment of wastewater since it binds to heavy metals and they can be extracted from the water.

In 2010, the *Journal of Experimental Biology* published some promising results where chitosan was injected into the damaged spinal cord of guinea pigs. It was found that electrical impulses would move through the spinal cord and the guinea pigs recovered movement. The research is in the very early stages; it has not yet reached human trials. Much more research needs to be conducted on dosage levels, whether recovery is temporary or longer lasting, and whether there are any long-term negative effects from this treatment. However, if successful, this could lead to an improved quality of life for people with spinal injuries.

Another new material is shrilk. It has been developed by scientists at the Wyss Institute for Biologically Inspired Engineering at Harvard University. Shrilk is also made from chitosan, a polymer developed from chitin from which the exoskeletons of crustaceans and insects are made, and fibroin, a protein derived from silk. The researchers looked at insects, not just for the materials but also for how to put the materials together. In insects, the chitin and fibroin are layered, so researchers layered the chitosan and fibroin to produce a material that is thin, clear, flexible and strong. A piece of shrilk is lighter but stronger than a comparably sized piece of aluminium. Due to the availability of chitosan and fibroin, shrilk is relatively cheap to manufacture and, importantly, it is biodegradable under conditions at landfill sites. The raw materials for making shrilk have already been approved by the Food and Drug Administration for use on humans. Potential uses include plastic bags, sutures that would dissolve over time and possibly as a scaffold for regenerating tissue.

The biggest difference between biopolymers and other polymers is that they are produced from biomass, rather than from petrochemicals. However, there are still many issues to be addressed with regards to biopolymers. Although starch-based biopolymers are produced from crops, the processing is still energy intensive; for example, for fertilising, harvesting, transporting and milling the crops.

Although many of the biopolymers are biodegradable, some, such as polylactic acid (PLA), require specific composting conditions for this to occur. Others such as PHB biodegrade in common natural environments. The other main issue with biopolymers is that they are much more expensive to produce. Most companies still manufacture polymers from petrochemicals and they still have a ready supply of chemicals needed for these processes to occur. Most biopolymers are only produced in small quantities, which are not economical at present.

ACTIVITY 4.15

BIOPOLYMERS

Aim

To research a biopolymer and link its structure to its properties and use(s)

What to do

1 Choose a biopolymer.

2 **a** Identify the monomer(s) that make up this biopolymer.
b Draw the structural formula for the monomer(s).
c Draw the structural formula for at least one unit of the biopolymer.
d Identify the properties of the biopolymer.
e Describe at least one use of the biopolymer and relate it to the properties of the biopolymer.
f Describe the properties of the biopolymer and relate them to the structure of the biopolymer.
g Explain whether your biopolymer can be used to replace an existing polymer produced from petrochemicals or whether it has a completely 'new' use.

3 Present your information as a video that can be uploaded to the class wiki or school intranet so that all members of the class can learn about different biopolymers.

4 Watch at least two other videos uploaded by members of your class and constructively critique the videos.

Biodegradable synthetic plastics

One major problem with synthetic polymers compared to natural polymers is that they are not biodegradable. This means that the plastics discarded into the environment or put into rubbish dumps are not decomposed naturally by the action of living organisms such as bacteria or fungi. Plastics comprise 4 per cent by volume of landfill and while natural polymers eventually decompose, the synthetic polymers stay around, contributing nothing but problems to the environment.

Figure 4.30 ▶ Plastic rubbish in the environment



Tetyana Kochneva/Dreamstime.com

BIODEGRADABLE PLASTICS

Visit this website to find out more about biodegradable plastics. Click on the Physical Science/Materials topics and find the article 'Managing packaging greener – biodegradable plastics'.

One solution to this is to make plastics that are biodegradable.

Synthetic biodegradable plastic materials do exist, and have found some application in packaging. For example, a photodegradable plastic is sometimes used for six-pack can carriers but there are still potential problems with biodegradable plastics. For example, a photodegradable plastic will not degrade if it is buried in a landfill where it is not exposed to light. When a biodegradable plastic decomposes, undesirable substances such as mineral fillers, metal salts or other potentially dangerous additives may enter the environment.

One approach to building biodegradability into synthetic polymers has been to alternate biopolymer sections with synthetic sections in the same polymer molecule. When the polymer is disposed of, microbes will attack the biopolymer sections, causing the polymer chain to be broken down into many smaller units. A method of doing this has already been developed.

Biodegradable rubbish bags have been made using a polymer that is made up of alternating segments of starch and ethylene. It is called a 'graft copolymer'. A stronger, stiffer rubbish bag, but one that is less biodegradable, can be made using cellulose instead of starch.

Another aspect of increasing the biodegradability is to add an 'environmental trigger'. The technique being researched is to add a catalyst to the starch molecule. The idea behind this is that when the rubbish bag is dumped into the environment, microbes release the catalyst as they consume the starch. This makes the bag decompose even more quickly.

The usual biological processes should then convert the remaining fragments of polyethylene into short hydrocarbon chains. The plastics don't disappear; they are simply converted to another form of matter.

The development of biopolymers and biodegradable plastics has been one way in which chemists have designed materials in response to environmental and economic issues.

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126) AC

▼ **Figure 4.31**
Close-up of biodegradable plastic taken by a scanning electron microscope. When the plastic is disposed of, granules of starch (orange) embedded in the plastic absorb water and expand. The plastic then breaks up, increasing the area in contact with bacteria in the soil, which digest the plastic.



Science Photo Library

CHAPTER SUMMARY

- Plastics are amazingly versatile materials. They can be as thin as a piece of food wrap or as strong as a bulletproof vest. They can be rigid enough to form car bumpers and aeroplane bodies or delicate enough to stitch a wound together. They can be woven into clothes, stuffed into sleeping bags or made into disposable nappies among a variety of things.
- Initially, natural starting materials were used to make the polymer, then chemists found that raw materials such as ethylene, propylene and benzene from crude oil provided more potential for chemical synthesis. The starting compounds are taken apart, rearranged and put together again.
- Some polymers are synthesised by addition polymerisation; others are synthesised by condensation polymerisation. Chemists have learnt to design polymers and there are endless possibilities for new polymers.
- One of the most useful features of plastics is also one of their biggest drawbacks – durability. Plastics last a very long time and this has led to problems of waste management. Chemists have developed solutions to this problem. One is to recycle the plastic so it can be used and reused. Another is to create a plastic that will break down over time.

CHAPTER GLOSSARY

addition polymerisation the process of polymer formation by molecules adding together without the loss of any atoms

amorphous substances that do not have an extended ordered arrangement of molecules

aramid a polymer containing amide linkages separated by a benzene ring

biopolymer a polymer made totally or in large part by living organisms

catalytic cracking the process in which high molecular weight (high boiling point) fractions from crude oil are broken into lower molecular weight (lower boiling point) substances

colloidal suspension tiny particles of solids dispersed through a liquid, which cannot be separated by filtration through filter paper

composite a material made up of two or more different materials

condensation polymer a polymer that forms by the elimination of a small molecule (often water) when monomers join together

condensation polymerisation the process of polymer formation by the elimination of a small molecule (often water) when monomers join together

conjugated alternating double (or triple) and single bonds

copolymer a polymer consisting of two or more different monomers

crystalline a substance with an ordered arrangement of atoms, ions or molecules in the solid

hydrophilic attracting water; 'water loving' and capable of forming bonds with water

hydrophobic more attracted to particles of the same type than to water, usually immiscible with water; 'water-hating' and cannot bond with or dissolve in water

latex a milky white liquid produced by some plants such as the rubber tree, which is used to make rubber

monomer a small molecule that combines with other monomers to make a polymer

myoglobin the oxygen-carrying protein used by mammalian muscle as a rapidly available source of oxygen

oxymyoglobin myoglobin protein that has reacted with oxygen

petrochemical industry industry that uses the components of crude oil (petroleum) as the starting material to produce a variety of different chemicals

plastic a material that is capable of being moulded by heat and pressure

plasticiser a small molecule inserted between polymer chains to hold them further apart

polyamide a polymer formed by a condensation polymerisation reaction between an amine group ($—NH_2$) and a carboxylic acid group (—COOH)

polyester a polymer formed by a condensation polymerisation reaction between an alcohol group (—OH) and a carboxylic acid group (—COOH)

polymer a substance consisting of long macromolecular chains

polymerisation a chemical reaction in which many small molecules combine to form one large molecule

semipermeable allows some substances to pass through but not others

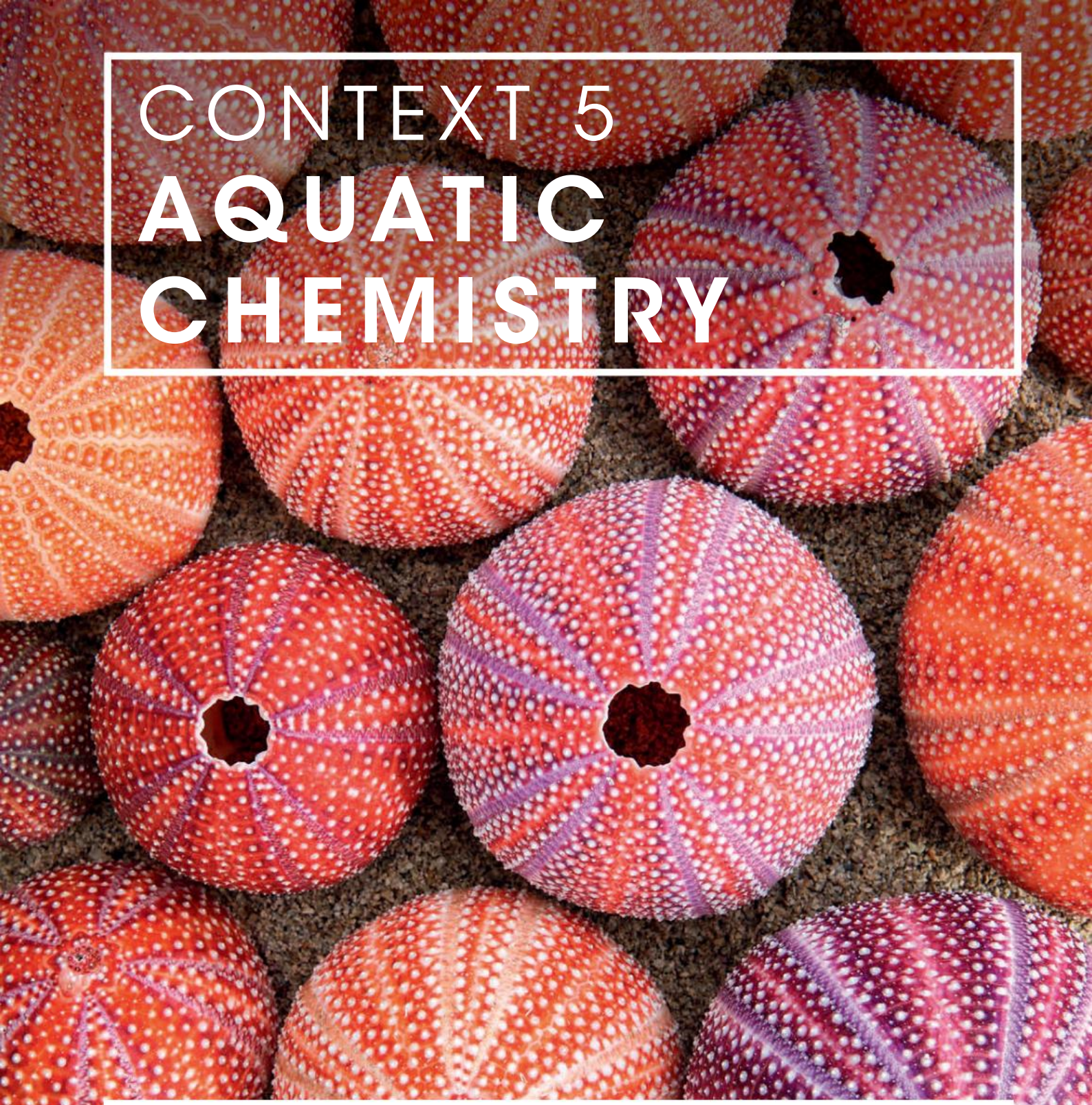
stabiliser a substance used to inhibit a chemical reaction

surfactant an agent such as a detergent that reduces the surface tension of liquids so that the liquid spreads out

thermoplastic a polymer that can be melted and reshaped

vulcanisation the process of strengthening a material such as rubber by combining it with sulfur and other additives and then applying heat and pressure

CONTEXT 5
AQUATIC CHEMISTRY



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By the end of this chapter you will have covered the following material.

Science as a Human Endeavour

- People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk (ACSCH085 AND ACSCH123)
- International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region (ACSCH087 AND ACSCH125)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCH088 AND ACSCH126)

Contextual story – Aquatic chemistry

- Aquatic environments involve many chemistry concepts.
- Gas solubility is affected by temperature.
- Carbon dioxide establishes an equilibrium in solution.
- Carbon dioxide levels affect pH and carbonate concentrations.
- Buffers are important to resist changes in pH.

Chemical understanding

- Equilibrium
  - equilibrium constant
  - effect of concentration and temperature
- Solubility
- Acid–base
  - pH
  - reactions
- Buffers

Investigations

Context 5

- Experiment 5.1 Uptake of carbon dioxide by aquatic plants
- Experiment 5.2 Effect of buffers
- Investigation 5.1 Effect of temperature on the solubility of carbon dioxide

Chapter 1

- Activity 1.1 Blue bottle experiment – a reversible reaction
- Activity 1.2 Calculating the equilibrium constant
- Experiment 1.1 Effect of changes to concentration on equilibrium
- Experiment 1.2 Changing the volume of a gaseous system at equilibrium
- Experiment 1.3 Effect of temperature on a system at equilibrium

Chapter 2

- Investigation 2.1 Percentage ionisation of a weak acid

Science as a Human Endeavour (SHE)

- People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk (ACSCH085 and ACSCH123)
- International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region (ACSCH087 and ACSCH125)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCH088 and ACSCH126)

Science Understanding (SU)

- Over time, physical changes and reversible chemical reactions reach a state of dynamic equilibrium in a closed system, with the relative concentrations of products and reactants defining the position of equilibrium (ACHSCH091)
- The effect of changes of temperature on chemical systems at equilibrium can be explained by considering the enthalpy changes for the forward and reverse reactions (ACSCH093)
- The effect of changes of concentration and pressure on chemical systems at equilibrium can be explained and predicted by applying collision theory to the forward and reverse reactions (ACSCH094)
- The effects of changes of temperature, concentration of chemicals and pressure on equilibrium systems can be predicted using Le Chatelier's principle (ACSCH095)
- Equilibrium position can be predicted qualitatively using equilibrium constants (ACSCH096)
- Acids are substances that can act as proton (hydrogen ion) donors and can be classified as monoprotic or polyprotic depending on the number of protons donated by each molecule of the acid (ACSCH097)
- The strength of acids is explained by the degree of ionisation at equilibrium in aqueous solution, which can be represented with chemical equations and equilibrium constants (K_a) (ACSCH098)
- The relationship between acids and bases in equilibrium systems can be explained using the Brønsted–Lowry model and represented using chemical equations that illustrate the transfer of hydrogen ions (ACSCH099)
- The pH scale is a logarithmic scale and the pH of a solution can be calculated from the concentration of hydrogen ions; K_w can be used to calculate the concentration of hydrogen ions from the concentration of hydroxide ions in a solution (ACSCH100)

Science Inquiry Skills (SIS)

- Identify, research, construct and refine questions for investigation; propose hypotheses; and predict possible outcomes (ACSCH074)
- Design investigations, including the procedure/s to be followed, the materials required, and the type and amount of primary and/or secondary data to be collected; conduct risk assessments; and consider research ethics (ACSCH075)
- Conduct investigations, including using volumetric analysis techniques and constructing electrochemical cells, safely, competently and methodically for the collection of valid and reliable data (ACSCH076)
- Represent data in meaningful and useful ways, including using appropriate graphic representations and correct units and symbols; organise and process data to identify trends, patterns and relationships; identify and distinguish between random and systematic errors, and estimate their effect on measured results; discuss how the nature of the procedure and the sample size may influence uncertainty and limitations in data; and select, synthesise and use evidence to make and justify conclusions (ACSCH077)
- Select, construct and use appropriate representations, including half-equations, balanced chemical equations, equilibrium constants and expressions, pH, oxidation numbers, standard electrode potentials and cell diagrams, to communicate conceptual understanding, solve problems and make predictions (ACSCH079)
- Communicate to specific audiences and for specific purposes using appropriate language, nomenclature, including scientific reports (ACSCH081 and ACSCH119)

Introduction



Tischenko Irina/Shutterstock.com

▲ **Figure 5.1**
There is a lot of chemistry happening in aquatic environments

There are many different **aquatic** environments – oceans, lakes, rivers, dams and aquariums. Chemistry plays an important role in each of these environments and affects the plants and animals that rely on these water sources.

In *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Context 3 and Chapter 6 you considered many aspects of water, including the importance of ice floating, what we find in water and why we feel cooler when water evaporates.

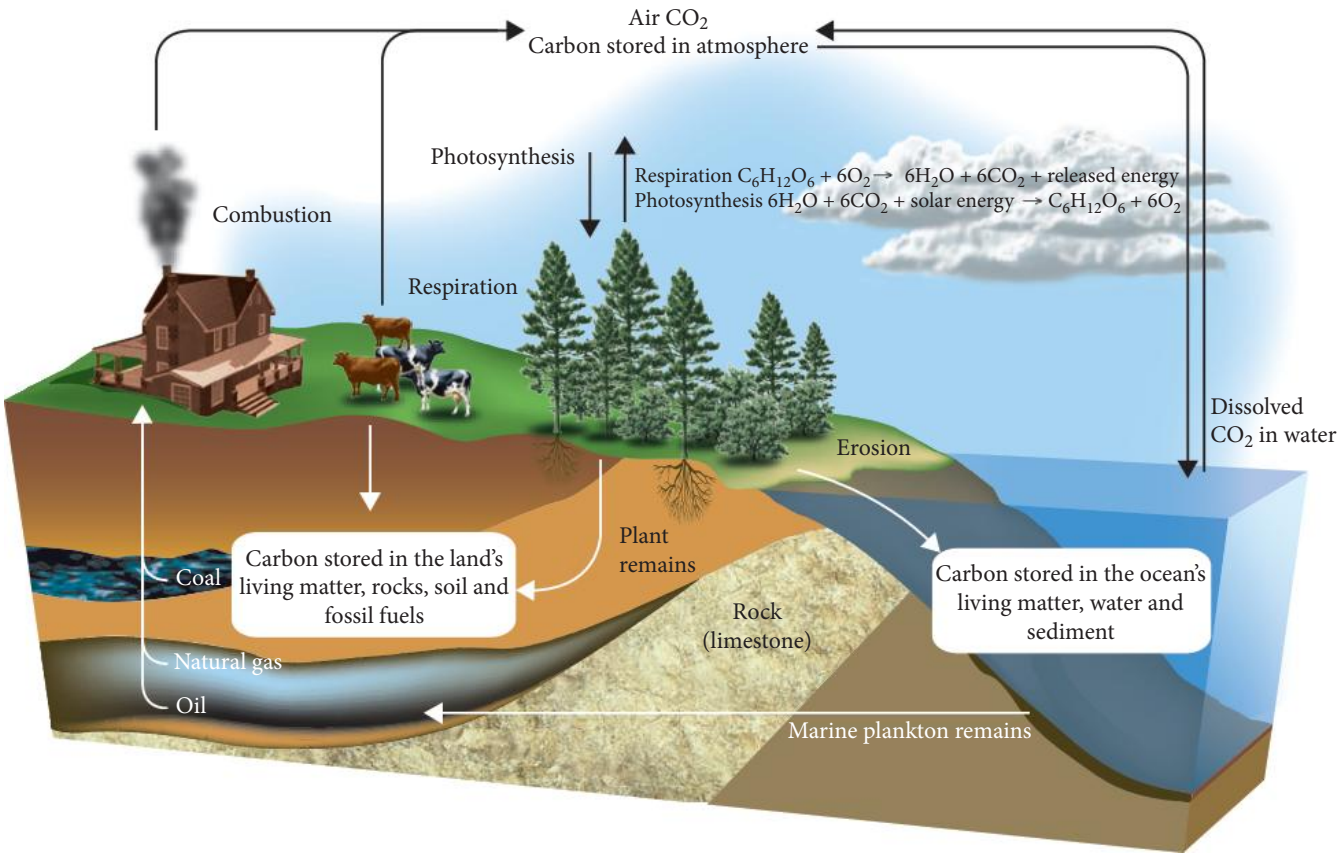
In this chapter, we will consider some other properties of water and solutions that affect aquatic environments. Many of these will involve carbon dioxide as it has a significant effect on many areas. This does not mean that other chemicals are not equally important. However, to cover all aspects is beyond the scope and time available in this chapter.

To revise the unique properties of water, refer to Nelson Chemistry Units 1 & 2 for the Australian Curriculum, *Context 3 and Chemistry Chapter 6, pages 57 and 257.*

Carbon cycle

Carbon goes through a cycle on Earth, moving between living organisms, dead organisms and inorganic compounds such as carbon dioxide. During **cellular respiration**, living organisms produce carbon dioxide gas. This is released into the **atmosphere**. Plants are then able to use the carbon dioxide in photosynthesis to produce sugars. These plants are eaten by animals, and the carbon is transferred and is then available to be used for cellular respiration. This is known as the **carbon cycle**.

▼ **Figure 5.2**
The carbon cycle



International collaboration is often required when investing in large-scale science projects or addressing issues for the Asia–Pacific region. (ACSCH087 and ACSCH125)

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126)

An important aspect of the carbon cycle is that some of the gaseous carbon dioxide dissolves in water. This means that the oceans and other water bodies are able to act as a store of carbon dioxide, reducing the amount of the gas in the atmosphere. It is also important for aquatic plants because plants that are fully immersed in water are unable to get the carbon dioxide needed for **photosynthesis** directly from the air.

Aquatic plants need carbon

You have probably learnt about how plants use photosynthesis to produce food in the form of glucose. In this process, the carbon in carbon dioxide becomes the carbon in glucose ($C_6H_{12}O_6$):

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

It is easy to see how this occurs in **terrestrial** plants where they are able to access carbon dioxide directly from the air. But what about aquatic plants?

Phytoplankton are one type of aquatic organism that has a very important role in the ecosystem. Although only very small individually, the vast number of phytoplankton means that they have a vital role in oceanic **food chains**. Some phytoplankton can use the energy in sunlight to facilitate photosynthesis. For this reason, they tend to live in the upper layers of the ocean or fresh water environments.

As phytoplankton are submerged in water, they are not able to access the carbon dioxide in the air for photosynthesis. Instead, they use the carbon in dissolved carbon dioxide or bicarbonate (hydrogen carbonate). This reacts to produce oxygen gas and food. When the phytoplankton are eaten by other organisms, the carbon is passed through the food chain.

Phytoplankton play a second role in removing carbon dioxide from the atmosphere. When phytoplankton die they sink to the bottom of the ocean, taking their carbon with them. This acts as a carbon store or sink. Over time, the dead phytoplankton decompose. However, it takes a very long time for the carbon to return to the atmosphere.

Figure 5.3 ▶
Phytoplankton



D. P. Wilson/Flpa/Minden Pictures/National Geographic Creative

Carbon dioxide in water

When we consider the structure of carbon dioxide, we would predict that it would be insoluble in water. You will remember from Unit 2 that carbon dioxide is a linear, symmetrical, non-polar molecule. Therefore, it would only be able to form **dispersion forces** with water. These dispersion forces would not be strong enough to overcome the hydrogen bonding between water molecules and so you would assume that carbon dioxide would be insoluble.

However, carbon dioxide actually has a solubility of 1.45 g L^{-1} at 25°C. This tells us that there must be some other contributing factors. The solubility is actually due to the **equilibrium** established between the gaseous and aqueous carbon dioxide:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

Some of the aqueous carbon dioxide will react with the water molecules to produce carbonic acid. And some of the carbonic acid will react to form hydronium ions and bicarbonate ions. Each of these reactions is reversible and therefore equilibrium is established:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

From this equation, it would be reasonable to predict that the concentration of hydronium and bicarbonate ions would be the same. However, some of the hydronium ions will react with carbonate ions producing bicarbonate ions. This will result in an increase in bicarbonate ions and a decrease in hydronium ions.



▲ **Figure 5.4**
Structure of carbon dioxide showing the valence electrons of carbon and oxygen



For more on reversible reactions and equilibrium, refer to Chemistry sections 1.2 and 1.3, pages 143 and 146.

EXPERIMENT 5.1

UPTAKE OF CARBON DIOXIDE BY AQUATIC PLANTS

When carbon dioxide dissolves, the solution becomes acidic. In this experiment, you will start with three bottles with carbon dioxide dissolved in water. An indicator will be used to ensure that they all have the same pH. You can then use the change in pH, seen through the change in colour of the indicator, to show a change in the amount of dissolved carbon dioxide.

Aim

To observe the effect of photosynthesis by aquatic plants on the dissolved carbon dioxide concentration

Materials

- 50 mL bottles or flasks with caps (any material)
- Drinking straw
- Pipette or medicine dropper
- Universal indicator
- Distilled water
- Scissors
- Aluminium foil or black paper
- Table lamp (optional)
- Several stems of *Cabomba* or similar aquatic plant
- Camera

Complete the risk assessment box to show any risks associated with completing this experiment and ways to manage them.

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals could splash in your eyes.	Wear safety glasses at all times.

Procedure

1. Half fill the three bottles with distilled water.
2. Add approximately 10 drops of universal indicator to each of the bottles. Ensure that the green colour of all three bottles is the same.
3. Use the straw to blow into each of the bottles until the colour changes to yellow and no further colour change occurs.
4. Take a photo to record the initial colour of the bottles.
5. Carefully cut 20 fronds of the *Cabomba* (or similar aquatic plant). Place the same number into each of two of the bottles. The third bottle is used as a control.
6. Place the caps on all of the bottles.
7. Totally cover one of the bottles with the *Cabomba* with foil or black paper so that no light can enter the bottle.

8 Place all of the bottles where they are exposed to light; for example, a windowsill or under a lamp.
9 Leave the bottles for a couple of hours.
10 Observe the colour of each of the bottles. Take photos of each and compare these to the initial colour.

Results

Download or print your photos in colour and organise these into a table to show the change in colour. Alternatively, describe the colours in your results table.

Analysis of results

1 What is the approximate pH of a solution when the colour of universal indicator is:
   a green?
   b red?
   c yellow?
2 What happened to the pH of the solution in each of the bottles?
3 What does the change in pH of the uncovered bottle with *Cabomba* tell you about the amount of dissolved carbon dioxide?
4 Account for the different results in the covered bottle.
5 Was there any change in the control bottle? Explain why this is so.

Discussion

1 What trends do your results indicate?
2 How can these results be applied to aquatic environments?
3 What changes could you make to increase the accuracy of the experiment?

Conclusion

What conclusion can you make about the effect aquatic plants have on dissolved carbon dioxide?

Increased carbon dioxide levels

WHERE DOES THE EXTRA CARBON DIOXIDE COME FROM?

Visit this website to see the distribution of sources of carbon dioxide in different countries.

Human activities often result in the production of carbon dioxide, which is then released into the atmosphere. For example, the **combustion** of petrol in cars and the use of electricity produced by the burning of coal both produce carbon dioxide, while the clearing of forests reduces the amount of carbon dioxide used in photosynthesis.



FTonline digitale Bildagentur GmbH/Alamy

Figure 5.5 ▶ Human activity has increased the production of carbon dioxide

Although this gas enters the atmosphere, it also has an impact on aquatic environments. If there is an increase in carbon dioxide gas, then the forward reaction in the **dissolution** of carbon dioxide will be favoured, producing more aqueous carbon dioxide:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

This will then affect the equilibrium in the reaction of carbon dioxide with water:

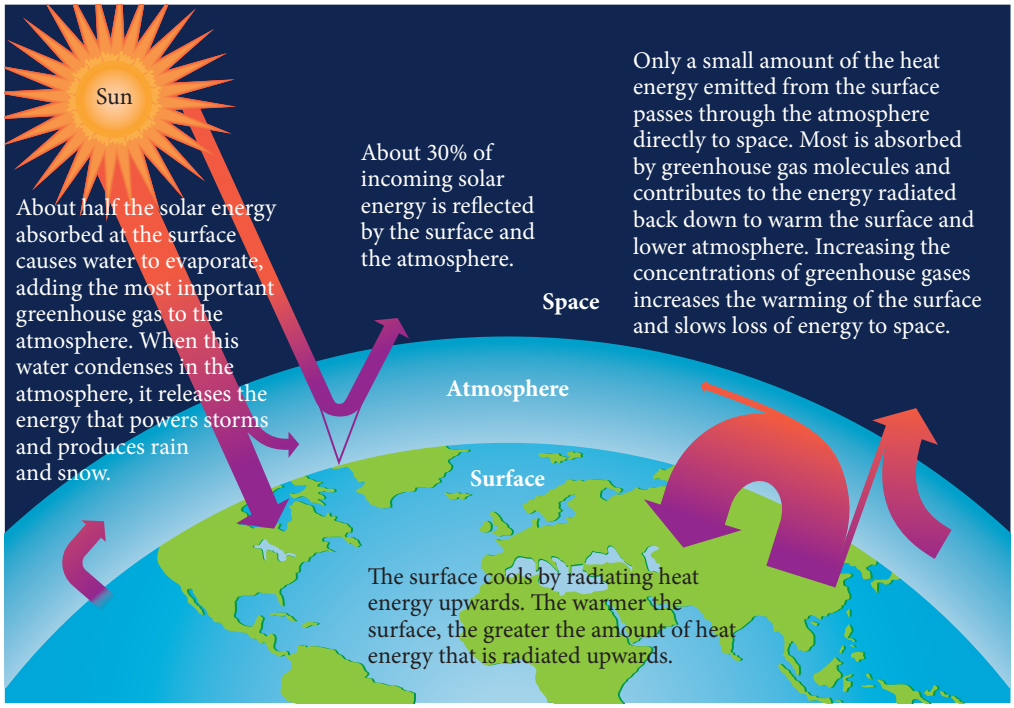
$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

The increased concentration of aqueous carbon dioxide favours the forward reactions. This results in an increase in the production of bicarbonate and hydronium ions. Therefore, an increase in carbon dioxide will lead to an increase in the acidity of the solution or body of water due to the increased concentration of hydronium ions.

Enhanced greenhouse effect

We often hear about how carbon dioxide is leading to **global warming**. This is due to carbon dioxide acting like a greenhouse and trapping the Sun's energy in Earth's atmosphere. While we need this to occur to maintain an adequate temperature, excess carbon dioxide has led to the **enhanced greenhouse effect**. In this situation, carbon dioxide dissolving in water bodies such as the oceans reduces the negative effect of excess carbon dioxide. When some of this excess carbon dioxide dissolves in the oceans and other water bodies, there is less in the atmosphere. If this did not occur, then the effect on global climate would be even greater.



The Intergovernmental Panel on Climate Change (IPCC) is an international body developed in 1988 to provide a clear, scientific view on climate change. It is open to all member countries of the United Nations (UN) and the World Meteorological Organization. The IPCC provides rigorous and balanced scientific information to decision makers. This level of knowledge is respected due to the range of scientists contributing and the review process of their contributions. Why do you think it is important that the IPCC completes objective and thorough assessments of climate change information?

In 1992, Australia and 150 other countries signed the United Nations Framework Convention on Climate Change at the United Nations Conference on Environment and Development held in Rio de Janeiro, Brazil. The countries identified the importance of working to find solutions to the emission of greenhouse gases to reduce climate change. This commitment was extended in 1997 with the Kyoto Protocol, an international agreement to setting emission reduction targets. The first commitment period from 2008 to 2012 saw 37 industrialised countries commit to reducing greenhouse gas emissions to an average of 5 per cent below 1990 levels. This was amended for the second commitment period from 2013 to 2020 to 18 per cent below 1990 levels.

For more information regarding equilibrium and the effect of concentration on the position of equilibrium, refer to Chemistry section 1.3, page 153.

◀ **Figure 5.6**
The greenhouse effect

People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk. (ACSCH085 and ACSCH123) AC

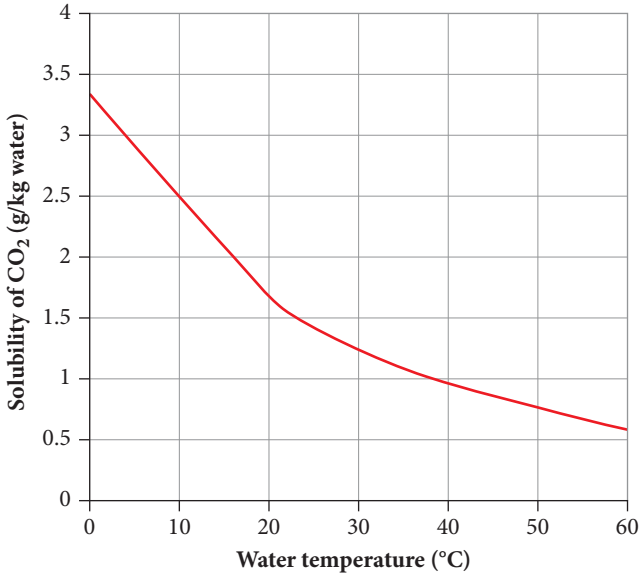
DIAGRAM OF ENHANCED GREENHOUSE EFFECT

Visit this website to see a diagram comparing the greenhouse effect with the enhanced greenhouse effect.

IPCC

Visit this website for more information on the IPCC.

Figure 5.7 ▼ The effect of temperature on the solubility of carbon dioxide



Unfortunately, the political and economic nature of this topic has meant that so far there has been little progress.

Effect of temperature on solubility

The **solubility** of gases depends on temperature. This is because as the temperature increases more carbon dioxide molecules have enough energy to overcome the forces of attraction with the water molecules and escape as a gas, leaving less aqueous carbon dioxide.

There are several impacts of this effect on carbon dioxide concentrations. The first involves the distribution of aqueous carbon dioxide on a global scale. Water bodies in colder climates will have a greater concentration of aqueous carbon dioxide than in warmer climates. Similarly, there will be more carbon dioxide dissolved during winter than during summer.

Another consequence is the impact on aquatic plant life. As the global temperatures increase, there is less dissolved carbon dioxide available for aquatic plants. This in turn may affect the rate of photosynthesis. However, in reality, there are usually other factors that limit the growth of aquatic plants before the carbon dioxide concentration takes effect.

INVESTIGATION 1.1

EFFECT OF TEMPERATURE ON THE SOLUBILITY OF CARBON DIOXIDE

What is your aim?

What do you want to achieve in your investigation?

What will you need?

Carefully consider all materials and apparatus that you will need to conduct your investigation. Show these in a clear, detailed list.

What are the risks?

Complete the risk assessment box before proceeding with your investigation.

What are the risks in doing this investigation?	How can you manage these risks to stay safe?

How will you carry out your investigation?

When designing your procedure consider factors such as:

1 What is your source of carbon dioxide?

2 How will you introduce the carbon dioxide to the water?

3 How will you ensure there are equal amounts of carbon dioxide gas initially?

4 How will you measure the amount of carbon dioxide that dissolves?

Outline your procedure in logical, clear, numbered steps.

What results will you collect?

What data will you need to be able to achieve your aim?

How will you analyse your results?

How will you calculate the amount of dissolved carbon dioxide in each of the different temperatures?

What have you found?

How much carbon dioxide was dissolved at each temperature?

What do you conclude?

What have you found regarding the effect of temperature on the solubility of carbon dioxide?

Ideas for improvement

How could you improve the investigation so that the results are more accurate?

Taking it further

How could you further investigate the concept of the effect of temperature on solubility?

Building shells

Many aquatic organisms rely on shells or skeletons for structure and protection.

As you have seen previously, carbon dioxide will react with water to produce hydrogen carbonate and hydronium ions:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

The hydrogen carbonate ion is able to further react to form carbonate and hydronium ions:

$$HCO_3^-(aq) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

If there are calcium ions available in the solution, then they will combine with the carbonate ion to form insoluble calcium carbonate. This provides the minerals that give shells and skeletons their strength:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$$

Although calcium carbonate is regarded as insoluble, in reality a very small amount is able to dissolve. This reaction is a reversible reaction, so, for the solid to form, the system must be at equilibrium and therefore a saturated solution is needed. If the solution is not **saturated**, then the **reverse reaction** (as written above) is favoured and thus any solid formed simply dissolves to form ions again.

It may seem unlikely that a saturated solution is able to be achieved in an ocean. However, as calcium carbonate has such a low solubility, it does occur. This can be reflected in the very low **equilibrium constant**:

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$
$$K = [Ca^{2+}] \times [CO_3^{2-}]$$
$$= 5.0 \times 10^{-9} \text{ at } 298 \text{ K}$$

Therefore, if the concentrations of the two ions are equal, the solution will be saturated when their concentrations are $7.07 \times 10^{-5}\,\text{mol}\,L^{-1}$. Any excess ions will be able to form the solid calcium carbonate needed for the shells, coral and skeletons of aquatic organisms.

▼ **Figure 5.8**
All of these shells contain calcium carbonate.



Karl Martila/Alamy

For more information regarding equilibrium constants (K), refer to Chemistry section 1.2, page 143.

For more information on acidity and pH, refer to Chemistry section 2.1, page 172.

Effect of carbon dioxide on shells

You already know that an increase in carbon dioxide in the atmosphere will lead to an increase in dissolved carbon dioxide. You also know that the dissolved carbon dioxide will react with water to form hydronium ions. Therefore, an increase in the amount of carbon dioxide will result in a more acidic solution.

With an increase in acidity, the hydronium ions react with the carbonate ions and reduce their concentration. This means that the solution is no longer saturated and the calcification and thus the formation of the shells and skeletons are interfered with.

This problem has been observed particularly in coral reefs. Coral forms a calcified skeleton. However, increased acidity is hindering this calcification. It is estimated that coral in the Great Barrier Reef has decreased by 50 per cent over the last 27 years. Acidification is one factor contributing to the decline. This reduces the amount of coral directly, but it also weakens the skeleton and makes the organism more susceptible to storm damage and erosion.

CHANGE IN pH OF OCEANS

Visit this website to see a diagram showing the change in pH of the oceans.

THINNING SHELLS OF OCEAN CREATURES

Read more about how increased carbon dioxide is causing a problem with the shells of ocean creatures.

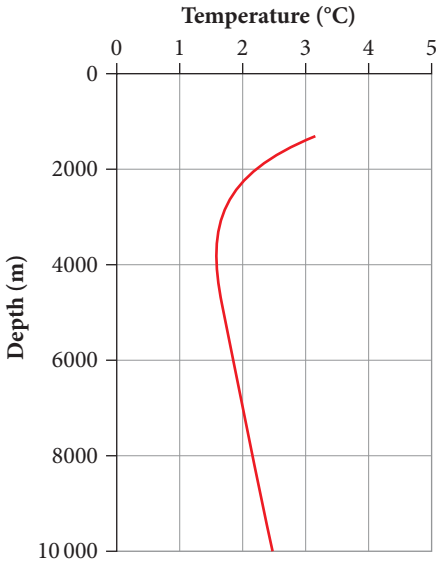


Figure 5.9 ▶ Temperatures at different depths of the ocean

Effect of temperature on shells

So far you have learnt that:

- calcium carbonate is only able to form a solid when the solution is saturated
- the concentrations needed for a saturated solution will depend on the value of K for the dissolution of the solid.

As the temperature decreases, the value of K for $CaCO_3$ dissolving will increase. This means that a higher concentration of calcium and carbonate ions is needed before the solution is saturated.

This trend will affect the shells and skeletons of aquatic organisms in colder waters. These waters may be in winter, in colder areas such as Antarctica or in the depths of deep water bodies. At these lower temperatures, the solid calcium carbonate is either unable to form or structures that have formed will dissolve. This phenomenon affects the type of organisms that can live in these colder environments.

Keeping a balance

It is important that environments meet the needs of the organisms that live there. This means that important conditions such as pH, concentration of ions and temperature are maintained at suitable levels. In a natural environment, the levels of a particular environment will dictate what organisms are able to survive. For example, freshwater fish, such as the Murray cod, need to live in water with low concentrations of salt. However, marine fish, such as the clownfish, need to live in water with a higher salt concentration. In aquariums, it is important that you maintain the correct levels.

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126) AC

Buffers

The health of organisms living in aquatic environments is pH dependent. This may be a direct effect or an indirect one due to the effect of pH on the toxicity of metals, ammonia and carbonate structure formation. Therefore, it is important to maintain the pH in an optimal range. In sea water the pH is approximately 8.3, whereas in fresh water the pH is lower, approximately 5.5–7.0.

Buffers are utilised in the natural environment as well as in aquariums to maintain an optimal pH. A buffer is a solution of a **weak acid** and its **conjugate base** (or vice versa) that is able to resist a change in pH when an acid or base is added. It achieves this due to the



Richard Whitcombe/Shutterstock.com

◀ **Figure 5.10**
Aquatic organisms need their environment to maintain a balance.

equilibrium established between the weak acid (or base) and the conjugate base (or conjugate acid). When an acid or base is added, the equilibrium will shift to counteract the addition. The concentration of hydronium returns to close to the original concentration and therefore the pH will remain constant.

In sea water, the buffer is due to bicarbonate and carbonate ions. In this case, the bicarbonate is the weak acid and the carbonate is the conjugate base. This sets up the following equilibrium:

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

When an acid is added to the solution (or ocean), the concentration of hydronium ions increases. According to **Le Chatelier's principle**, this leads to the reverse reaction being favoured to counteract the change. As the reverse reaction uses up hydronium ions, their concentration decreases, which means that the pH remains close to its original value despite the addition of an acid.

Alternatively, when a base is added to the solution (or ocean), it will react with the hydronium ions, neutralising them. This causes a decrease in their concentration. According to Le Chatelier's principle, the **forward reaction** will be favoured to counteract this change. The forward reaction produces hydronium ions; therefore, the pH will remain close to its original value despite the addition of a base.

The breakdown of organic matter and fish waste causes the water to become more acidic. The buffer is able to counteract this change so that the pH is not affected. Calcium and magnesium ions cause the water to become more alkaline. This happens when items such as shells are added to the environment. However, the buffer is able to counteract this change and maintain the original pH. Therefore, the solution (or ocean) is able to maintain a constant pH even if an acid or base is added.

Natural sea water has a pH of 8.0–8.3. At this pH, there are approximately equal amounts of bicarbonate and carbonate ions. This is the ideal situation because it allows the buffer to effectively counteract the addition of both acids and bases. The **buffer capacity** is the amount of the acid or base that can be added without a significant change in pH. The buffer capacity is greatest when there are equal number of moles of the weak acid and the conjugate base. This is because it is able to counteract the addition of both acids and bases. The buffer capacity is also affected by the actual amount of the weak acid and conjugate base. The more of each is present in the solution, the greater the buffer capacity. This is because there are more reactants and products present; therefore, both the forward and reverse reactions can occur to a greater extent to counteract the addition of acids and bases.

For more information about equilibrium and shifts in equilibrium in response to changes, refer to Chemistry section 1.4, page 154.

For more information about conjugate pairs, refer to Chemistry section 2.1, page 178.

For more information on Le Chatelier's principle, refer to Chemistry section 1.4, page 162.

For more information about buffers, refer to Chemistry section 2.6, page 199.

BUFFER CAPACITY

Visit this website for more information about buffering capacity.

EXPERIMENT 5.2

EFFECT OF BUFFERS

A buffer consists of a solution of a weak acid and its conjugate base (or vice versa). In this experiment, we will use a buffer solution composed of acetic acid, which is a weak acid, and acetate, which is the conjugate base.

Aim

To compare the behaviour of a buffered solution with an unbuffered solution

Materials

- 4 × 100 mL beaker
- 50 mL measuring cylinder
- Stirring rod
- 2 plastic droppers
- 10 mL of 1 mol L^{-1} acetic acid (CH_3COOH)
- 40 mL of 1 mol L^{-1} sodium acetate (CH_3COONa)
- 30 mL of 0.1 mol L^{-1} hydrochloric acid (HCl)
- 30 mL of 0.1 mol L^{-1} sodium hydroxide (NaOH)
- Distilled water
- Universal indicator

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
0.1 mol L^{-1} HCl is corrosive to skin and clothes.	Wear gloves and an apron.
0.1 mol L^{-1} NaOH is corrosive.	Wear gloves and an apron.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Measure 10 mL of 0.1 mol L^{-1} acetic acid (CH_3COOH) and pour it into a clean, dry beaker.
2. Measure 40 mL of 0.1 mol L^{-1} sodium acetate (CH_3COONa) and add this to the acetic acid in the beaker.
3. Divide this solution evenly into two beakers.
4. Add 5 drops of universal indicator to both beakers. Record the colour, and therefore pH, of the solutions. Label these beakers 'Buffered solution'.
5. Into a third beaker add 50 mL of distilled water.
6. Add 10 drops of universal indicator to the water.
7. Add hydrochloric acid drop by drop to the water until the colour is the same as the buffered solution.
8. Divide the solution from step 7 evenly between two beakers. Label these beakers 'Unbuffered solution'. Record the colour of these solutions.
9. To one of the buffered solutions add 0.1 mol L^{-1} HCl one drop at a time until 40 drops have been added. Stir the solution between each drop.
10. Record the colour and pH of the resultant solution.
11. Repeat steps 9 and 10 for one of the unbuffered beakers.
12. Repeat steps 9–11 with the remaining beakers, adding 0.1 mol L^{-1} NaOH instead of HCl.

Results

Copy and complete the following results table.

Beaker	Initial colour	Initial pH	Final colour	Final pH	Change in pH
Buffered solution + 0.1 mol L^{-1} HCl					
Buffered solution + 0.1 mol L^{-1} NaOH					
Unbuffered solution + 0.1 mol L^{-1} HCl					
Unbuffered solution + 0.1 mol L^{-1} NaOH					

Analysis of results

1 Describe the pH change for each of the beakers.
2 Describe the difference between changes in the buffered and unbuffered solutions.
3 Use your understanding of equilibrium to account for these changes.

Discussion

1 Suggest what would happen if you continued to add HCl to the buffered solution.
2 Suggest what would happen if you continued to add NaOH to the buffered solution.
3 What is the effect of having a buffer in the solution?
4 In what ways may the experiment be improved to provide more accurate results? Explain how each of your suggestions would facilitate this improvement.

Conclusion

What conclusion can you make regarding the action of a buffer in a solution?

Taking it further

1 Your teacher may allow you to test the effect of adding more acid or base to the buffered solution to test your hypothesis.
2 How could you further test the effect of buffers?

CHAPTER SUMMARY

- The carbon cycle allows the movement of carbon through the environment, including aquatic environments.
- Some carbon dioxide is able to dissolve in water: $CO_2(g) \rightleftharpoons CO_2(aq)$
- Plants need dissolved carbon dioxide for photosynthesis.
- Carbon dioxide reacts with water, establishing an equilibrium with carbonic acid and bicarbonate ions:

  $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

  $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$
- The enhanced greenhouse effect is due to an increase in greenhouse gases such as carbon dioxide. The increase in atmospheric carbon dioxide leads to an increase in dissolved carbon dioxide.
- Carbon dioxide solubility decreases with an increase in temperature.
- Carbonate ions are produced from bicarbonate ions. These form insoluble calcium carbonate, which is important in the formation of the shells and skeletons of aquatic organisms.
- An increase in carbon dioxide leads to an increase in acidity of the solution. This reacts with the carbonate ions, leaving fewer ions for the formation of shells and skeletons.
- As temperature increases, a higher concentration of calcium and carbonate ions are needed for the formation of shells and skeletons.
- Buffers are solutions of a weak acid and its conjugate base, or vice versa, that are able to withstand the addition of an acid or a base. A carbonate/bicarbonate buffer can maintain a near-constant pH in aquatic environments.

CHAPTER GLOSSARY

aquatic relating to water

atmosphere the gases surrounding Earth

buffer a solution of a weak acid and its conjugate base (or vice versa) that can counteract the addition of an acid or a base to maintain a constant pH

buffer capacity the extent to which a buffer is able to counteract the addition of an acid or a base

carbon cycle the movement of carbon through the environment

cellular respiration the chemical reaction occurring in cells where oxygen and glucose react to form carbon dioxide, water and energy

combustion reacting with oxygen

conjugate base (of an acid) the base that is formed when an acid donates a proton to a base

dispersion force a weak intermolecular force resulting from the temporary attraction between adjacent molecules

dissolution the process of dissolving

enhanced greenhouse effect the trapping of excess heat in Earth's atmosphere due to increased production of greenhouse gases such as carbon dioxide through human activity

equilibrium the state for a reversible reaction in a closed system when the forward and reverse reactions occur at the same rate

equilibrium constant (*K*) the value of the ratio between the concentration of the products and reactants

food chain a series of organisms that depend on the previous one as a food source

forward reaction the process of the reactants forming the products

global warming the gradual increase in the overall temperature of Earth's atmosphere

Le Chatelier's principle a principle that predicts the effect of changes to a system at equilibrium: if a change is made to a system at equilibrium, the system will react to partially counteract the change

photosynthesis the process whereby organisms, particularly green plants, can use sunlight to produce nutrients (sugars) from carbon dioxide and water

phytoplankton microscopic organisms that float in large numbers in fresh or salt water

reverse reaction the reaction in which the products form the reactants

saturated a solution that contains the maximum amount of the substance dissolved in the solvent (usually water)

solubility the amount that is able to dissolve in a given volume of the solvent (usually water)

terrestrial relating to land

weak acid an acid in which only a small proportion of the molecules will donate their proton; the K_a is small

CONTEXT 6
MOLECULAR MANUFACTURING



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By the end of this chapter you will have covered the following material.

Science as a Human Endeavour

- The acceptance of scientific knowledge can be influenced by the social, economic, and cultural context in which it is considered (ACSCH084 and ACSCH122)
- People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk (ACSCH085 and ACSCH123)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCH088 and ACSCH126)

Contextual story – Molecular manufacturing

- Medical uses
- Materials production
- Uses in energy production

Chemical Understanding

- Nanotechnology
- Protein structure and synthesis
- Enzymes
- Nanoparticles
- Batteries/fuel cells/solar cells

Investigations

Chapter 10

- Activity 10.1 Modelling dipeptides

Science as a Human Endeavour (SHE)

- The acceptance of scientific knowledge can be influenced by the social, economic, and cultural context in which it is considered (ACSCH084 and ACSCH122)
- People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk (ACSCH085 and ACSCH123)
- Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability (ACSCSH088 and ACSCH126)

Science Understanding (SU)

- Fuel cells can use metal nanoparticles as catalysts to improve the efficiency of energy production (ACSCH109)
- Organic materials, including proteins, carbohydrates and synthetic polymers display properties including strength, density and biodegradability that can be explained by considering the primary, secondary or tertiary structures of the material (ACSCH129)
- Organic molecules, including polymers, can be synthesised using addition and condensation reactions (ACSCH136)
- Molecular manufacturing processes, including protein synthesis, involve the positioning of molecules to facilitate a specific chemical reaction; such methods have the potential to synthesise specialised products (for example, carbon nanotubes, nanorobots, chemical sensors used in medicine) (ACSCH138)

Science Inquiry Skills (SIS)

- Select, construct and use appropriate representations, including physical, virtual and graphical models of primary, secondary and tertiary structures, structural formulas, chemical equations, systematic nomenclature (using IUPAC) conventions and spectra, to communicate conceptual understanding, solve problems and make predictions (ACSCH117)
- Communicate to specific audiences and for specific purposes using appropriate language, nomenclature, genres and modes, including scientific reports (ACSCH119)

Molecular manufacturing and society



To learn more about molecular manufacturing, refer to Chemistry section 10.1, page 432.

Molecular manufacturing is an advancing branch of chemistry. It uses different chemical techniques and processes to control how a chemical is formed. We can join chemicals in specific ways to get a desired product, or even manipulate individual atoms to build up a structure or chemical.

Many fields of science use molecular manufacturing. These include the medical field with products being used to diagnose and treat disease, deliver drugs to precise sites within the human body and even perform surgeries on the nanoscale inside the human body. Many new materials are being produced, including smart materials that are water resistant, scratch proof, unusually durable or strong, or ultraviolet resistant. The production of fuel cells, batteries and solar panels is being advanced every day due to the precise construction of materials using these processes. A range of products already in use can be seen in Figure 6.1.

The manufacturing process of these products is very complex. Each product is made by a number of different processes, involving chemical reactions that are closely controlled.

The simplest way to synthesise a desired molecule is to line up large reacting molecules in a specific orientation so that the right functional groups or reactive sites react together. This is known as the orientation effect.

Another simple chemical method is the use of protecting groups. This allows chemists to protect reactive sites or functional groups that they do not want taking part in a reaction. This avoids unwanted side reactions that would result in undesired products.

In *Nelson Chemistry Units 1 & 2 for the Australian Curriculum*, you learnt about how the properties of materials at the nano level are different from those in the same element or compound at the macro level. Nanotechnology involves the use of nano-sized particles and structures to gain special properties. Some molecular manufacturing involves the use of nanotechnology to manipulate atoms at the atomic level. This allows chemists to build nanostructures such as nanosensors and nanobots.

▼ **Figure 6.1**
A range of products is now made by molecular manufacturing: a) sunscreen, b) solar cells and c) fabrics.



Marlin Shields/Alamy

hxdyl/Shutterstock.com

Liam Grant/Alamy

Medical uses

An area of molecular manufacturing that nanotechnology is advancing quickly is medicine. Scientists are producing nanomachines, surgical tools and systems to deliver drugs. The aim of using molecular manufacturing and nanotechnology in medicine is to diagnose and treat patients more efficiently and effectively with fewer side effects. The use of specifically created molecules and nanoparticles allows targeting of specific cells and areas inside the human body due to their physical shapes or ability to bind to specific molecules.

The Protein Data Bank (PDB) is a database that is helping scientists make these specific molecules. The bank is an online storage site for information on the structure and function of a range of biological molecules, including proteins and nucleic acids. The PDB can be accessed by anyone. This information allows scientists to create specifically shaped molecules for use in medicine. Knowledge of biological molecule structure is very important as it is the structure of a protein that determines its function.

Diagnosis and assessment tools

Diagnosis and treatment of medical conditions have high levels of risk associated with them. Conditions often take time to develop inside the human body, and by the time they are detected, it is sometimes too late to cure them, or the only treatments available are extreme and have negative side effects.

Conventional medicine has a range of tools to assess diseases and medical conditions. These are extremely effective when symptoms are visible on the macro or whole body scale. However, many medical conditions result in changes on the atomic and molecular level in the human body. These molecular changes are difficult to detect and assess accurately and often it is too late when the disease becomes detectable on the macro scale.



APPLICATIONS OF NANOTECHNOLOGY

Use the interactive to create a short presentation or poster on an area of research and innovation.

PROTEIN DATA BANK

Visit this website and search for information on specific proteins. Try entering the search term 'haemoglobin' and explore the information given to you about its structure and function.

To learn about different methods for producing specific molecules such as proteins, DNA structures and carbon nanotubes, refer to Chemistry sections 10.2 and 10.3, pages 435 and 444.

Molecular manufacturing and nanotechnology has allowed the design and building of tools that can assess and evaluate chemical changes as a result of medical conditions before they become too advanced. Diseases can be treated earlier, reducing the level of risk for the patient. Atomic manipulation and the orientation effect are used to build molecules and chemical structures with a particular shape that can be used for a range of purposes.

Nanosensors/biosensors

A **biosensor** is a structure that can detect a change in a biological component such as a particular chemical. It can also be used as a measurement device. A **nanosensor** is a sensor that is nanosized. Biosensors can detect when a particular chemical is present in the blood or body. Specific chemicals can indicate when a particular disease is present.

For example, cancer cells produce specific chemicals that indicate when a tumour is present. Bacteria and viruses do the same. A biosensor can detect these chemicals and indicate if any of these are present. One of the major advantages of a biosensor over conventional tests is that the assessment of the patient and detection of the problem can occur much earlier. This reduces the risk to the patient as the disease can be treated early before the disease has time to develop fully.

An example of better monitoring leading to reduced risk in patients is in the assessment of patients with diabetes mellitus. Sufferers produce ketones as their blood insulin decreases. Propanone (acetone) is one of these ketones and is usually detected in the urine of a patient. A nanosensor called a cantilever, seen in Figure 6.2, has a particular structure that will bind with the acetone in the air as a patient breathes out. The cantilever structure is covered with molecules that recognise and bond to the ketone molecules produced by a patient with diabetes mellitus.

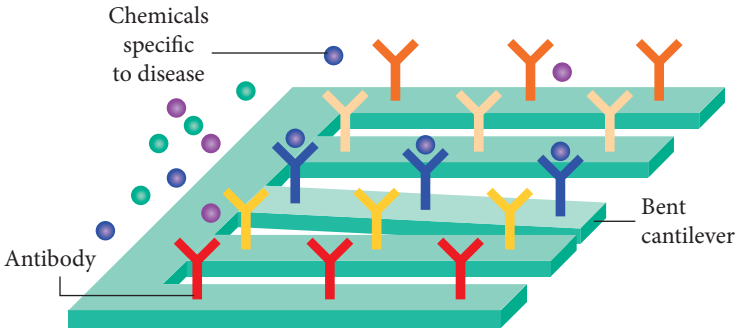


Figure 6.2 ▶ A bent cantilever due to bonding of particles to the antibodies on the surface

When the cantilever binds to the acetone, the structure changes due to the extra molecules now bound to the surface. As it is a nanosensor, it has useful nanoproperties. As the cantilever changes shape, it generates a small electrical charge that can be measured and used to determine the concentration of acetone present. The more molecules present, the more the cantilever is bent out of shape, and the larger the electrical charge generated. In this way, the amount of molecules present can be measured.

The cantilever itself is manufactured on the atomic level so that it has the specific shape seen in Figure 6.2. It appears like a series of diving boards with each 'board' able to move independently. Cantilevers can be made of materials such as silicon, or from polymers. Both structures are manufactured with a specific shape by using methods such as atomic manipulation. In this process, atoms are added together in a particular arrangement to give a final structure that has the required electrical conductivity property needed for sensing.

People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk. (ACSCH085 and ACSCH123) AC

This cantilever has a number of advantages over conventional detection of ketones. First, the patient only needs to breathe on the sensor rather than provide a urine sample. Second, the cantilever can detect acetone in much smaller amounts than conventional tests. This allows doctors to identify anomalies in blood glucose much earlier than previously, thus reducing the overall risk to the patient, who can adjust their blood glucose concentration before symptoms appear.

Cantilevers have also been developed to detect bacteria, viruses and fungal spores. Antibodies with a specific shape on the surface of the cantilever bond to the bacteria, virus or spore. An antibody is a molecule that uses molecular recognition. An antibody is specific for a particular molecule or structure. So if the sensor is going to be used to detect the chemicals associated with bacterial or viral infection, the antibody needs to be able to recognise that molecule. An antibody is a protein and can be produced through artificial protein synthesis so it has the required shape to bond only to the chemicals that need to be detected.

To learn about how molecular recognition occurs in enzymes, refer to Chemistry section 10.3, page 444.

Smart drugs

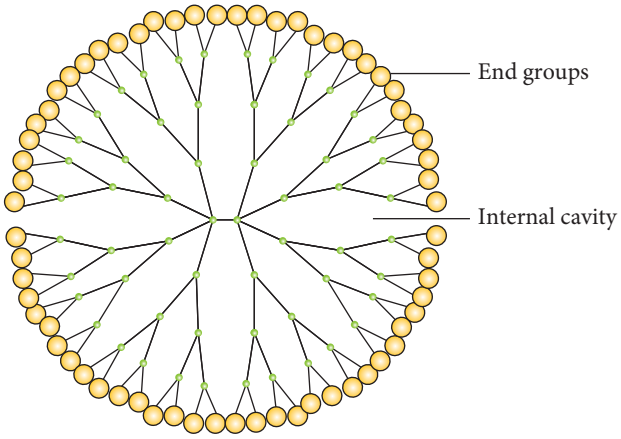
Conventional medicine involves a patient taking a drug in tablet, liquid or injectable form. The drug then moves to the affected area and performs its task. This results in several problems, the major one being side effects. Many drugs are potent and often affect parts of the body that were not supposed to be targeted. These side effects increase the level of risk to patients and can often make them sicker as a result.

Assessment and evaluation of the risks involved in drug delivery has led to the development of smart drugs. A smart drug is one that that can be targeted to a particular site in the body. Nanoparticles and nanostructures such as **dendrimers** can be built that can carry drugs to the part of the body where the disease is located, and deliver the drugs only to that site. This increases the efficiency of the drug because it is not wasted on healthy parts of the body, and it also minimises side effects in the patient. The end result is reduced risk to the patient during treatment.

Dendrimers

Dendrimers are used to carry drugs around the body and deliver them to where they are needed. A dendrimer is a molecule built with a specific shape that can contain or bond to the drug they will carry. Reacting molecules are arranged in a specific orientation so that when they react they form a particular final structure. They must be highly branched but regular, meaning the branching occurs at specific points, not at random.

Some dendrimers (Figure 6.3) are synthesised with a cavity that is filled with the drug to be delivered. To create this structure, the molecules that react together must be oriented correctly so that the desired reactive sites come into contact. If the molecules are oriented correctly, then the final molecule has the required regular structure. If the reactants do not line up, then the branched structure does not form and the final molecule is not suitable for drug delivery.



▲ **Figure 6.3**
A dendrimer showing the internal cavity to hold drugs to be delivered

Other dendrimers carry drugs by bonding the drug molecules to specific functional groups that are engineered onto the dendrimer molecule. This technique involves manipulation of bonding between molecules. Depending on the structure of the drug, molecules with the appropriate functional groups are selected to be placed onto the dendrimer. To do this, the polarity of the molecules is considered. If the drug that needs to be carried has polar functional groups, the molecules on the dendrimer need to be able to form bonds with polar molecules. A non-polar dendrimer would be unable to bond to a polar drug so would be unable to transport it around the body.

As dendrimers need to go to different parts of the body depending on the drugs to be delivered, scientists must consider properties like solubility. For a dendrimer to be water soluble so it can dissolve in the bloodstream, the end groups (Figure 6.3), would be made of a polar or ionic reactive group so it could form hydrogen bonds or ion–dipole bonds, making the entire structure soluble. If this dendrimer was to be fat soluble, the end groups would be non-polar so it would dissolve in other non-polar substances.

Dendrimers are already being used in many medical applications. They are used to diagnose heart muscle damage and as a glue to seal lacerations in the cornea of the eye. Dendrimers are also used to deliver antimicrobial drugs around the body to fight bacterial and viral infections.

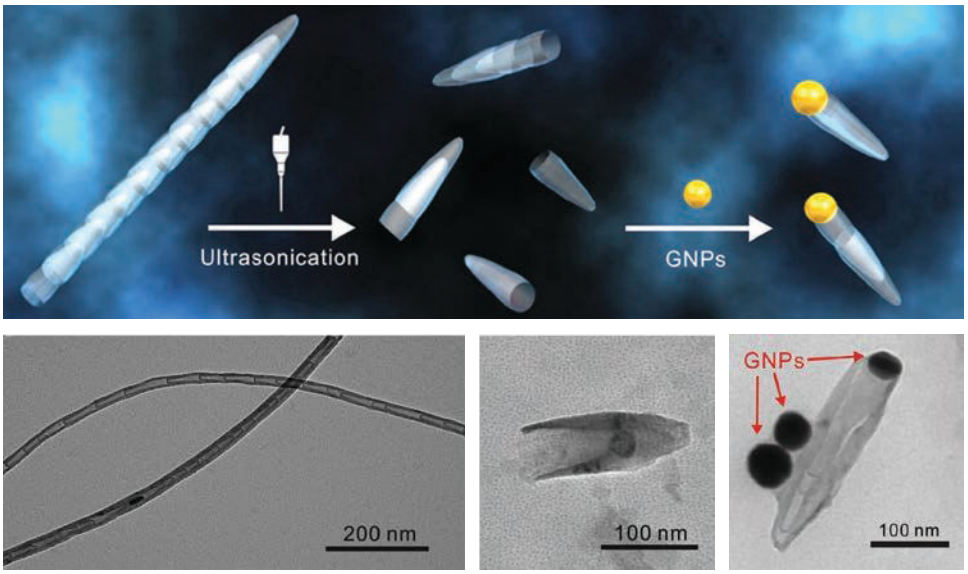


To learn how molecules with specific functional groups are produced, refer to Chemistry section 10.4, page 448.

Nanoparticle corked carbon nanotubes

In Year 11, you learnt about the unique properties that carbon nanotubes have due to their nanosized structures. Carbon nanotubes can have other atoms incorporated into them. A common element included in the basic carbon structure is nitrogen. The resulting nanotube is said to be nitrogen-doped. One method of creating these structures is to use atomic manipulation, which allows substitution of one atom for another. Nitrogen can also be added during the production process so that it is incorporated in the structure as it forms.

Nitrogen-doped carbon nanotubes have been created with a hollow structure, closed at one end that can be filled with drugs. The **nanocup** (Figure 6.4) that is formed is then corked with a gold nanoparticle so the drugs do not escape the nanotube.



Reprinted (adapted) with permission from Zhao, Y., Tang, Y., Chen, Y. & Star, A. (2012) 'Corking Carbon Nanotube Cups with Gold Nanoparticles'. ACS Nano. American Chemical Society, 6(8), 6912-21.

Figure 6.4 ▶
A carbon nanotube 'nanocup' with gold nanoparticle (GNP) corking

The ability to manipulate atoms to make whatever shapes are required is vital in the construction of these nanocups. Manipulation of how the atoms are added means multiple nanotubes are grown in a cup shape, stacking together in a similar way to a stack of plastic cups. The stack of nanocups that are formed can be seen in Figure 6.4. To fill them with the required drugs, the nanocups are separated, drugs are injected, then gold nanoparticles that exactly fit the hole are introduced and they attach to the nanotube.

To deliver the nanocups to the desired site in the body, either molecular recognition or manipulation of bonding is used. Viruses, bacteria or diseased cells in the body release specific chemicals. The nanocups are designed to find and bond to these chemicals, triggering a release of the drugs that they contain. The chemicals being targeted might be polar, non-polar or ionic, or may be able to bond to antibodies, similar to the method discussed earlier. Scientists select appropriate functional groups, molecules or antibodies to attach to the carbon nanotube that then 'seek out' the target chemicals.

This allows the nanocup to be delivered to the site in the body where the drugs are required. Because only the specific site of the disease is targeted, the risk to the patient of side effects and damage to healthy cells and tissues is reduced.

To learn about how nanoparticles are produced, refer to Chemistry section 10.3, page 444.

Therapy

Molecular manufacturing and nanotechnology is being developed to improve conventional therapies. Targeting therapy at the cellular level by attempting regrowth and repair of damaged individual cells is something that cannot be done with conventional medicine.

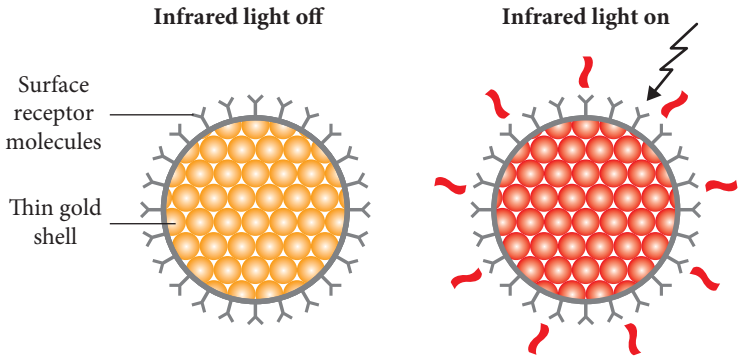
Chemotherapy

Nanoparticles are being investigated as a treatment for cancer as they can be delivered to the site of the cancerous tumour and then stimulated to kill the cancer cells. These nanoparticles are made from ordinary chemicals such as gold, carbon and iron oxide, but their nano size gives them a specific and useful property.

Iron oxide nanoparticles, gold nanoshells and carbon nanotubes can convert electromagnetic energy into heat. When the nanoparticles reach the site of the cancer, the body is irradiated with laser light or a magnetic field. This is mostly harmless to the rest of the body, but it causes the nanoparticles to generate heat between 40°C and 45°C, which kills the cancer cells. This is targeted at the cancer cells and will not affect surrounding cells, reducing the risk of side effects of conventional radiation therapy. The structure of such a nanoparticle can be seen in Figure 6.5.

Tissue engineering

Some medical conditions result in destruction of tissues such as muscle and heart tissue. There is risk to the patient in terms of organ function or mobility issues when this occurs. Tissue engineering



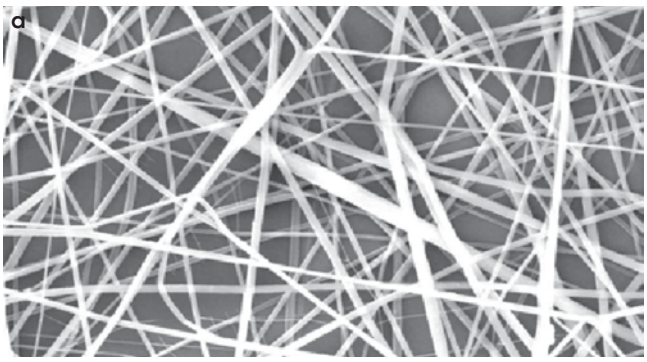
◀ **Figure 6.5**
A nanoshell producing heat when exposed to infrared light to destroy cancerous cells

aims to use carbon nanotubes and other nanoparticles to replace or restore the structure and function of damaged tissues. Scientists are investigating how biomaterials can be used on the atomic level to rebuild or replace damaged structures. While there are some risks in using artificial materials inside the human body due to possible adverse reactions, this needs to be balanced with the risks associated with non-functioning tissue and the effect this can have on the quality of life.

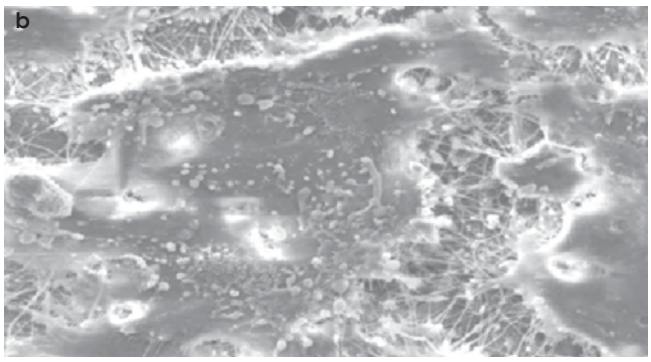
The biomaterials used can be permanent, usually when a tissue needs to be replaced. They can also be biodegradable, so they will break down and be removed from the body after a period of time, which reduces the risk of adverse reactions as the materials spend less time in the body.

The materials produced need to have different properties depending on what tissue they are trying to replace or repair. Carbon nanotubes are very strong and are being investigated as scaffolding, to hold structures in place while they grow. Picture a building under construction. The scaffolding around the outside of the building helps the builders to position materials and ensure the building is built correctly. The scaffolding nanomaterials do the same thing. They make sure the tissue grows in the correct shape and structure. Figure 6.6 shows a carbon nanofibre mat (left) used as a scaffolding to grow tissue over. The final tissue is seen on the right.

▼ **Figure 6.6**
a) A carbon nanofibre mat; b) a tissue growth scaffold



Venugopal, J. et al. (2007). Biocomposite nanofibres and osteoblasts for bone tissue engineering. *Nanotechnology*, 18(5), 1–8. doi:10.1088/0957-4484/18/5/055101



Venugopal, J. et al. (2007). Biocomposite nanofibres and osteoblasts for bone tissue engineering. *Nanotechnology*, 18(5), 1–8. doi:10.1088/0957-4484/18/5/055101

Materials production

Molecular manufacturing and nanotechnology are being used to create materials that have different and important properties. Materials can be strong, flexible, corrosion resistant, water repellent, more durable and more effective. A material can be 'made to order' with any properties that someone would like. Many materials produced through these processes are already available and many others are under development.

A variety of molecular manufactured structures such as carbon nanotubes and nanoparticles have been incorporated into different materials such as fabrics and structural materials to give them special and unique properties. These properties have significant economic benefits for companies as they can reduce the amount of material used to make a product, and many of the materials are more environmentally sustainable as less non-renewable materials such as petroleum are used in favour of natural materials.



To learn about how carbon nanotubes are built and their properties, or how nanoparticles are produced, refer to Chemistry section 10.3, page 444.

Fabrics and textiles

The basic fabrics that you wear every day are composed of natural and synthetic polymers. The natural polymer cellulose makes up cotton and rayon. Synthetic polymers include polyester

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126)

and nylon. All these polymers are long chains that are bundled to form fibres that are then woven into fabrics for use in clothes, sheets, curtains, pencil cases and many other objects.

Natural fibres have useful properties, including water absorbency, are usually softer and allow air flow. Synthetic fibres are often stronger and more durable but are not as soft or comfortable as natural fibres. No matter whether natural or synthetic fibres are used, there are environmental impacts. Natural materials such as cotton require large amounts of water to grow, while many synthetic materials are made from petroleum-based products, which are non-renewable. Improvement of fibres, both natural and synthetic, can lead to reductions in the use of materials and this can have a positive environmental impact.

Making fabrics stronger

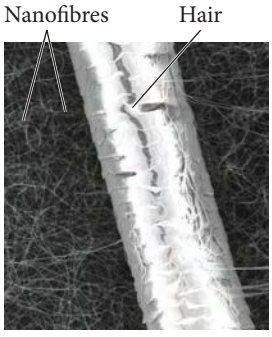
Molecular manufacturing can build long carbon nanotubes that can be incorporated into fibres to increase their strength and durability. Carbon nanotubes have exceptional strength for their density. They are very light, and very strong.

Clothes that contain carbon nanotubes would take much longer to wear out, as the fibres would be less likely to break. A carbon nanotube is about 200 times stronger than rayon but only one-third the density. Fabrics produced with carbon nanotubes are stronger and lighter than conventional fabrics. This means that one of the problems with natural fabrics can be overcome. Natural fabrics can be made stronger, and still retain their advantages over synthetic fibres such as breathability and softness. Reducing the use of petroleum products to create synthetic fibres can help to conserve this non-renewable resource.

However, the methods that are normally used to create carbon nanotubes do not work when trying to combine them with polymer fibres. Normally, to grow a carbon nanotube, carbon is added atom by atom to a structure. This is not suitable for the production of polymer fibres. Scientists have developed a new method of atomic manipulation that uses carbon nanotubes to create fibres of poly(vinyl alcohol) (PVA) that are among the strongest and most durable synthetic fibres created.

In the past, small carbon nanostructures have been added to the finished material, giving some extra strength. This new method uses nanotubes as a nucleation material. This means the nanotubes are used to help grow the PVA fibre in an extremely structured and ordered manner. The PVA and carbon nanotubes are repeatedly heated and cooled. The PVA forms on the ordered nanotubes, creating fibres that are perfectly aligned with one another. This fibre is unusually strong and durable due to its ordered structure.

Nanofibres



Revolution Fibres Ltd. www.revolutionfibres.com

Figure 6.7 ▲ A human hair surrounded by nanofibres

Nanofibres can be developed by a process called **electrospinning**. It uses the electrostatic properties of a fibre to separate extremely fine fibres from a polymer solution. You can see nanofibres next to a human hair in Figure 6.7. Nanofibres have a large surface area and a small pore size. Many nanofibres have already been produced with useful and different properties:

- Nylon nanofibres – these nanofibres are only 10–50 nm thick. Their most useful property is that they are hygroscopic. They can attract and hold water in large amounts, which is useful where a fabric needs to be water absorbent.
- Polyester nanofibres – these nanofibres are only 60 nm thick. They also absorb water. Polyester nanofibres can absorb about 30 times more water than regular polyester nanofibres.
- Luminescent nanofibres – a combination of polyester and nylon nanofibres is used as each has different optical properties. They reflect light of only a specific wavelength, so only one colour is seen. This changes when you view the fabric from a different angle. This fabric appears to change colour depending on how light shines on it, and how the observer is viewing it.

People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk. (ACSCH085 and ACSCH123)

Military fabrics

In the past, soldiers have worn heavy, restrictive body armour. While it protects the soldier, it severely restricts movement, which can lead to other problems such as the inability to move quickly when under attack. The United States military is developing smart clothing that can change its properties when a soldier is struck. The armour contains nanoparticles that group together when a soldier takes a strike. The grouped nanoparticles make the fabric stronger and stiffer. This reduces the forces that act on the soldier, so injuries are less severe.

Other nanoparticles in fabric help with camouflage. Some nanoparticles are pigments that can move around the fabric, changing how the fabric appears and helping camouflage the soldier as conditions change.

These strange properties are due to the nanosize of the particles being used. Nanoparticles often have different properties from macro-sized particles. These nano properties are often unique to nanoparticles and allow innovative materials to be produced.

Scientists at the Massachusetts Institute of Technology are working on a fabric that can monitor the condition of a soldier. The fabric would then change its structure to help with the problem that the soldier has. One fabric has particular fibres that can store heat when the body is producing excess heat. This can then be passed back to the soldier when their body temperature drops. The fibres use the conductive properties of carbon nanotubes, which can both absorb and conduct heat.

Temperature control is important for a soldier, as a change in body temperature can lead to problems with concentration and judgement. A soldier who is affected by heat can be a danger to other soldiers. So controlling a soldier's body heat reduces risk to the individual soldier and the entire unit.

The same fabric is also designed to create an instant solid cast when a soldier needs to immobilise a body part. A fluid containing nanoparticles is a part of the fabric and when the soldier turns on a power supply, the nanoparticles change the fabric from a flexible material into a solid cast to keep a broken bone or other injury protected.

The nanoparticles are designed to respond to an electrical or magnetic field. When the power supply is turned on, it sends an electrical signal that causes the nanoparticles to assemble and create a solid material. This process of self-assembling completely changes the structure of the material. Self-assembly means the particles line up in a specific arrangement that allows intermolecular bonds to form. The more bonds that form between molecules, the more solid the material becomes. When the electrical signal is turned off, the particles disassemble, the intermolecular bonds break and the fabric becomes more flexible again.



To learn about how molecular self-assembly of particles can occur, refer to Chemistry section 10.3, page 444.

Water-repellent fabrics

Water-repellent fabrics can be manufactured by manipulating the intermolecular forces between molecules or by use of nanoparticle coatings.

One of the simplest ways to repel water is to use a surface coating that does not allow bonding to water. Molecules are manufactured to contain specific non-polar functional groups on the surface, packed very closely together. This has two effects. First, the water cannot bond to the non-polar functional groups so remains beadlike on the surface of the material, as seen in Figure 6.8. Second, the construction of the material surface means that the functional groups are packed very closely together and water molecules cannot pass through the gaps and into the material fibres.

A fabric can also be coated with a layer of nanoparticles that also repel water. Because the nanoparticles are so small, they pack together much closer than the particles in any other material. This close packing of the particles means nothing can get through them and onto the fabric. This includes bacteria, dirt particles and water. The water will form beads on the surface because it is not absorbed into the fabric (Figure 6.8). As the water is on the surface with dirt and other particles, when the water is wiped away or poured off, it will take the dirt with it. This makes these fabrics very easy to clean. This type of material is already used in clothes and outdoor materials such as shadecloths and tents.



Vinogradov Ilya/Shutterstock.com

▲ **Figure 6.8**
Water-repellent fabric works because of the nanoproperties of the material.

Self-healing structures

Molecular manufacturing and nanotechnology have the ability to make materials 'self-healing'. When materials become scratched or damaged, they can repair themselves.

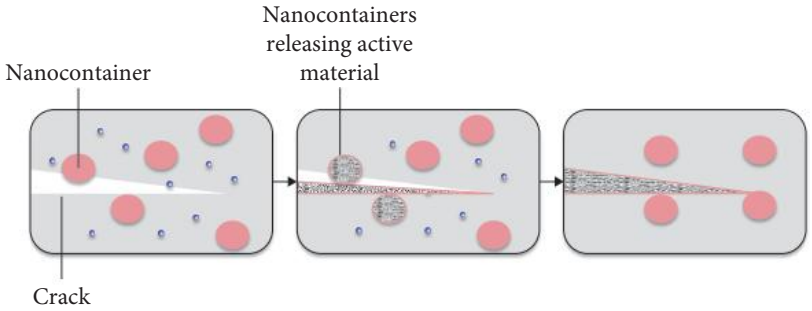
Spacecraft, medical devices such as pacemakers inside the body and many electronic components are replaced when they sustain damage. This presents a level of risk for the users of these objects. It is obvious that the failure of a pacemaker would increase the risk of heart failure for the patient. Damage to the space shuttle and satellites have resulted in failures of materials that in the most extreme case caused the crash of the space shuttle Columbia. Damage to the heat-resistant tiles allowed failure of the materials upon re-entry into the atmosphere. The ability of these materials to self-heal could greatly reduce the risk of these types of accidents.

A self-repairing material would give materials a longer lifespan, reducing the need for costly replacements. This would also save on the amount of materials used, as replacement structures would not need to be built as often, so less metals, plastics and fuels would need to be used.

Using atomic manipulation, scientists have been able to grow nanocontainers made of nanoparticles of titanium dioxide, TiO_2, silica and various polymers. The nanocontainers must have a particular shape and size to fit into the material without affecting the function of the material. The precise addition of individual atoms means the structure has a specific final shape. A polymer container is constructed as described previously, by ensuring correct orientation of the reactant molecules.

These **nanocontainers** are around 300–400 nm in diameter and fit between the molecules and atoms of the material structure. The containers are filled with an active material that is released to perform a task. Active materials can include adhesives to repair cracks, polymers to reinforce a structure, lubricants, metal particles or corrosion inhibitors. A material containing nanocontainers is shown in Figure 6.9.

Figure 6.9 ▶ Nanocontainers 'healing' a crack in a material. When they come into contact with the crack, they release their active material to fill in the crack.



To protect against corrosion, nanocontainers with corrosion inhibitors are incorporated into paints and coatings on metal structures. When the metal begins to rust, chemical reactions produce a pH change, which causes the nanocontainer to break and release the anti-corrosion chemicals.

This is an important application as $500 billion is spent worldwide each year preventing and treating corrosion and replacing structures affected by corrosion. Structures can fail due to corrosion of the metals and materials they are made from. There have been numerous cases of bridge and building failure due to corroded metal structural components.

Figure 6.10 ▼ The effect of corrosion on an oil platform can cost a company millions of dollars.



Calum Davidson/Alamy

One particular focus is on the oil and gas industry. Oil rigs and other structures are located far out in the open ocean, and are very difficult to repair. The damage corrosion can cause is seen in Figure 6.10. The microcapsules in a paint coating could provide better protection against corrosion of structures in an environment where it is difficult to access and treat them by conventional methods. The development of these anticorrosion materials will reduce the risks to the companies involved. Less damage due to corrosion will mean less down time for equipment and less money lost for the company.

Self-healing glass is also under development. When a windscreen on a car or a smartphone screen cracks, a polymer liquid from a nanocontainer could be released and fill in the cracks, allowing the user to keep driving the car or using the phone. This would also prevent the crack spreading, as is common in a windscreen.

WOW

Shine a light to repair a key scratch

Imagine you returned to your car to find a key scratch down the side. Conventional methods of scratch repair are expensive and time consuming. Scientists in Cleveland, Ohio, in the United States, have developed a polymer paint that can repair itself when ultraviolet light is shone onto it. Most paints are made of polymers that have long chains. This self-healing paint is composed of many short-chain molecules held together by metal ions that act like a glue. When the ultraviolet light is shone onto the paint, the bonds between the metal ions and the polymer weaken, and the polymer becomes a liquid. The liquid spreads out, filling in the scratch. When the ultraviolet light is turned off, the bonds strengthen and the liquid turns back into a solid paint. And your scratch is gone.

People can use scientific knowledge to inform the monitoring, assessment and evaluation of risk. (ACSCH085 and ACSCH123)

Structural materials

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126)

Across the world, the construction of houses, buildings and even whole cities is accelerating as the human population increases. The focus for many companies and governments is on sustainability. Many structures are built with energy-generating devices such as solar panels, or are built to reduce energy consumption. Another sustainability focus is on the materials used. Vast amounts of metals, concrete and glass are used in the construction industry each year. The use of molecular manufacturing and nanotechnology can help reduce the amount of materials used, or increase their lifespan. In the end, the result is the same, less material is needed and the industry becomes more sustainable.

Structural materials such as concrete, steel and glass can have their basic properties improved by addition of nanoparticles. Nanoparticles, with their extremely small size, can be incorporated into a material without disrupting the basic structure of the material. Then the unique properties of the nanoparticles can take effect, improving the properties of the material.

Concrete contains large grains of silica (SiO_2). When nanoparticles of silica are used in the concrete mix instead of large grains, the concrete packs more neatly. The concrete containing nano-silica is more durable and stronger because there is less space between particles in the concrete mix. The compressive strength of this concrete is three to six times higher than normal concrete. This means a smaller area of concrete can support a larger weight, so less concrete needs to be used.

To learn more about how nanoparticles are produced and used, refer to Chemistry section 10.3, page 444.

There are also significant risks involved with structural materials. Failures in steel and concrete can lead to building collapses, or they can be more easily damaged in natural disasters such as storms or earthquakes. The use of these altered materials can reduce the risk of failure, ultimately making buildings safer.

The nano-silica that is used in concrete also prevents water entering the concrete after it sets. One of the main reasons that concrete fails in buildings is that water inside the concrete structure causes it to weaken.

Fatigue is a common problem in steel (Figure 6.11). It occurs when steel is under pressure for a long time, such as in structural sections of buildings and bridges. Fatigue causes steel and other metals to fail due to sustained use.

Copper nanoparticles added to steel as it is formed makes the steel surface more even. The copper nanoparticles are small enough to fit between the atoms of iron and the other elements that make up the steel. Instead of having large spaces between atoms, the spaces are filled by the nanoparticles. This means less cracking occurs due to fatigue. The copper nanoparticles lengthen the life of steel, which makes buildings and other structures safer.

Steel often weakens and fails at weld points. When steel is welded, the joint is not as strong as the steel on either side. Many serious accidents have occurred due to failures of welded areas. To improve this strength, magnesium and calcium nanoparticles can be added to the material used to weld the steel together. The particles make the welding stronger and



Kypros/Alamy

▲ **Figure 6.11**
Metal fatigue can cause catastrophic failure of components.



B. A./Wikimedia Commons/CC-BY-SA-3.0

Figure 6.12 ▲
A failure in a welded joint in a metal rail

materials using these nanoparticles have had less structural failure. This makes structures safer and less likely to need repairing during its lifetime. Figure 6.12 shows how a welded joint can fracture.

Glass in high-rise buildings is often out of reach and hard to clean. In cities, pollutants such as bacteria and organic compounds from car exhausts coat windows. Glass that has a titanium dioxide nanoparticle coating can clean itself.

The titanium dioxide nanoparticles act as catalysts, causing the pollutants coating the windows to break down and form simple molecules that will wash off in the rain. What makes the titanium dioxide nanoparticles even better, is that they attract water. So when it rains, they attract water, which washes off the substances they have broken down.

Scientists have even developed fire-protective glass with a layer of silicon dioxide nanoparticles in between the regular glass panels. When heat is applied, the nanoparticles form a fire shield, blocking heat and light from passing through the glass.

Scientific knowledge can be used to develop and evaluate projected economic, social and environmental impacts and to design action for sustainability. (ACSCH088 and ACSCH126)

Uses in energy production

Energy production and sustainability is one of the major challenges facing the world. About 80 per cent of the world's energy is supplied by fossil fuels. These fuels are running out and are producing massive amount of pollutants. The use of fossil fuels is not sustainable, so alternatives are a major focus in the energy industry. Renewable alternatives such as wind power and geothermal energy are still under development but are not suitable for all energy applications. The development of alternative energy supplies that do not have the environmental impacts of fossil fuel burning is very important due to the problems associated with increased carbon dioxide in Earth's atmosphere.

Molecular manufacturing and nanotechnology have the ability to create smaller, more efficient solar panels, fuel cells and batteries. Use of nanoparticles and carbon nanotubes in components can speed up and control reactions, and produce larger amounts of useful energy from smaller devices.

These devices can be small enough to fit in phones and computers or larger for use in fuel cells, which could replace generators and provide the energy needed for a large building. These types of applications have potential to make the energy industry more sustainable.

To learn more about nanoparticles as a catalyst and the properties of nanotubes, refer to Chemistry section 10.3, page 444.

Batteries

Batteries are vital in our technological society, with laptops and smart phones useless without them. How many times have you heard someone wish their battery lasted longer? Many essential medical devices such as pacemakers and hearing aids also use batteries that need to have a long life. Molecular manufacturing and nanotechnology can produce batteries that are smaller, lighter and have a much longer life. Batteries can be made safer, with less chance of leaking, and less heat produced during operation and charging.

The use of nanoparticles and nanotubes in the form of electrode materials and electrolytes in conventional lithium ion batteries is already happening. Nanoparticles are especially useful as catalysts due to their large surface area to volume ratio. Carbon nanotubes are an excellent structural material as they have high strength, but low density. It is these properties that are most important in batteries and fuel cells.

Electrode materials

Anodes and cathodes are being made with nanocarbon structures such as carbon nanotubes and carbon aerogels. A gel is a material that is part liquid and part solid. It is fluid, but has many properties of a solid. An aerogel is an ultralight material in which the liquid part of the gel is

replaced by a gas. Aerogels are extremely light and have low thermal conductivity. The ultralight carbon aerogels reduce the weight of a battery or fuel cell, while their low thermal conductivity means they can withstand high temperatures.

These products have exceptional electricity conduction due to their nanostructure and can give a higher voltage or more sustained electricity production when used in the electrodes of a battery instead of traditional graphite.

- Silicon-coated carbon nanotubes used in anodes in lithium ion batteries increase the capacity of the battery around 10 times. The lifetime of the battery is thus significantly improved.
- A lithium ion battery that can recharge in 10 minutes is being developed by using silicon nanoparticles in the anode of the battery. Silicon nanowires in the anode increase the surface area available for reaction, allowing the lithium ions to move around more quickly, increasing the rate of the chemical reaction taking place.

Solid polymer electrolytes

Electrolytes in most batteries are a liquid as this is the best material for conducting the ions around the cell. The faster the ions are transported, the faster the charging and discharging of a battery. In a lithium ion battery, the electrolyte is commonly a lithium salt such as $LiPF_6$, $LiBF_4$ or LiClO dissolved in organic solvents.

There are many problems with liquid electrolytes such as this. They can leak if there is a problem with the battery, and these particular chemicals can be explosive if overheated. Solid electrolytes are much safer, but they do not provide the conductivity needed to make a battery efficient.

Liquid electrolytes can be replaced with polymer liquids and gels containing nanoparticles. These electrolytes are safer than those in conventional lithium ion batteries. They are not explosive and are closer in structure to a solid than a liquid. If the battery were to leak or overheat, it would be less dangerous for the user. These electrolytes are also more efficient at generating electricity as the nanomaterials are better at conducting electricity.



Caro/Alamy

▲ **Figure 6.13**
Batteries can leak their electrolyte, which can be dangerous.

Liquid electrolytes can also be replaced with solids by making the solid particles nanometre sized. A nanopowder containing lithium, tin, phosphorus and sulfur ($Li_{10}SnP_2S_{12}$) is under development. This solid nanopowder can conduct lithium ions at a rate equal to, or better than, traditional electrolyte liquids. In case of leakage, a solid is much easier and safer to deal with than a liquid electrolyte. Also, this material is not flammable, eliminating another problem of liquid electrolytes.

WOW

T-shirt batteries

Imagine plugging your mobile phone into your T-shirt to charge it up. Or having your smart phone or tablet screen part of the fabric that you are wearing.

Researchers are making fabrics that can do just that. Cotton fibres in material can be integrated with highly conductive carbon nanotubes so that the fibres in the material can store electricity and conduct electricity around the fabric. Cotton threads are dipped into a carbon nanotube ink and dried in an oven. When dried, the fibre is highly conductive and flexible and has similar material properties to the original cotton threads.

Another method is coating the fibres of the materials with a nanolayer of manganese(IV) oxide. The resulting material can store electricity. The fabric can be used to charge up a smart phone or tablet and then be recharged. This discharging and recharging can occur thousands of times for the same piece of fabric.

Solar cells

The acceptance of scientific knowledge can be influenced by the social, economic, and cultural context in which it is considered. (ACSCH084 and ACSCH122)

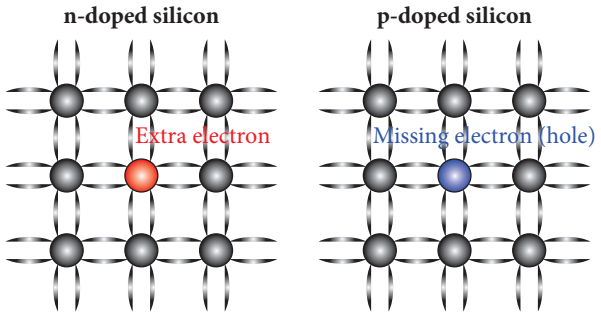
Many homes now have solar panels and solar hot water. As the technology used in solar panels has improved, it is now possible to have your whole house powered by them. In some situations, any unused electricity can be sold back to the power companies, making the householder a profit.

Solar panels have become more popular as power costs have increased. Fuel prices have increased and as companies are being made to deal with the carbon dioxide that they produce, these costs are being passed onto the consumer. Consumers are looking for ways to decrease their power bills, and have turned to solar panels. Many consumers also want to take some form of action to reduce the emission of carbon dioxide into the atmosphere and the negative effects that arise from this.

The creation of smaller, more efficient solar cells for a variety of uses is already underway. By using molecular manufacturing processes, solar cells can be made that:

- absorb more light
- are smaller so they can be carried around
- are flexible so they can fit any shape
- produce more energy than conventional solar cells.

Figure 6.14 ▼
The n- and p-type semiconductors



How a solar cell works

A solar cell converts light energy into electricity by using the photovoltaic effect. A solar cell is made of two layers called n-type and p-type semiconductors. Both are usually made from a silicon lattice with other atoms such as phosphorus and boron substituted into the silicon crystal structure. An **n-type semiconductor** has elements such as phosphorus added, which results in extra electrons being present in the material, free to move and not bonded to any atoms. A **p-type semiconductor** has an atom such as boron in the silicon structure so has a 'hole' where it is short of an electron. These two types can be seen in Figure 6.14.

These semiconductors are placed next to one another in a solar cell as seen in Figure 6.15. When light shines on the solar cell, the electrons from the n-type semiconductor move into the 'holes' in the p-type semiconductor. This movement of electrons and the charge differential that builds up generates an electric current.

Molecular manufacturing and nanotechnology can be used to make this process more efficient in a variety of ways.

Nanostructures such as carbon nanotubes can be incorporated into the solar cell. Carbon nanotubes are highly suitable for electricity production due to their extraordinary electrical conductivity properties. As they can conduct electricity better than other materials, there is more electron movement, so more electricity is produced for the same amount of light striking the solar cell.

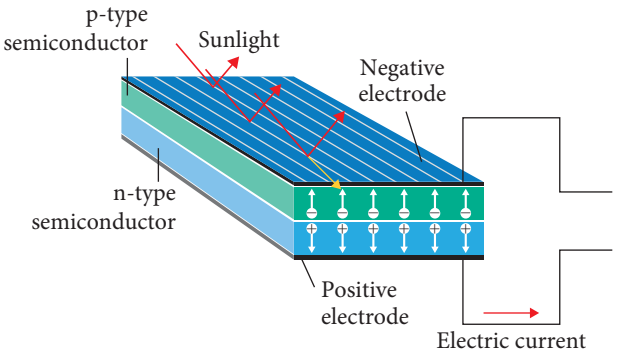


Figure 6.15 ▲
How a solar cell works when light shines on the cell: electrons move from the n-type to the p-type semiconductor, generating an electric current.

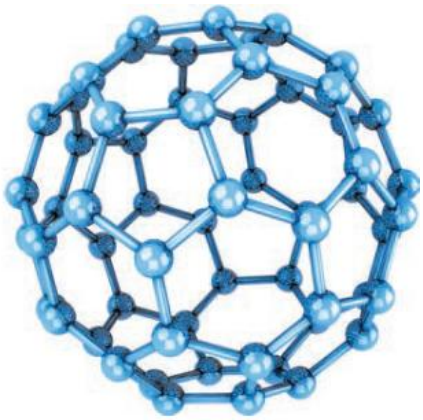
Nanoparticles also have properties that are extremely useful in a solar cell. Many nanoparticles can absorb more light than the same particles that are macro sized. More light absorbed means less reflection and less wastage of the incoming solar energy.

New materials such as polymers are being investigated to replace or work with the silicon structures. As silicon is expensive to produce and not readily available, this could make solar cells much cheaper.

Carbon-based solar cells

One of the special properties of carbon nanotubes is their excellent electrical conductivity. Use of these materials in solar cells allows electrons to be conducted much more efficiently than in conventional solar cells. Carbon nanotubes also absorb light very well, especially in the infrared, visible and ultraviolet region.

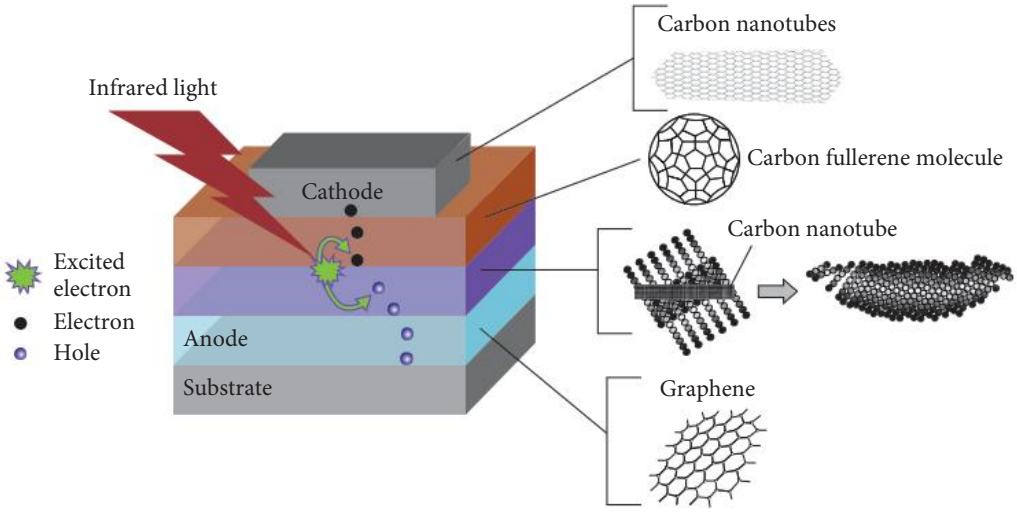
Other forms, or allotropes, of carbon can be produced by nanotechnology. A **fullerene** (Figure 6.16) has a structure similar to a hollow ball or a cage and has its own unique electrical conduction properties. Highly conductive **graphene**, a two-dimensional sheet of carbon, is also manufactured in a variety of shapes and structures. Each of these carbon allotropes has its own unique properties in terms of strength, density and electrical conductivity. Putting them together can make a solar cell that has more efficient electricity production.



Laguna Design/Science Photo Library

▲ **Figure 6.16**
A fullerene molecule

Solar cells have been made that use all three allotropes of carbon, along with selected other materials, to produce a highly efficient cell (Figure 6.17) for a fraction of the cost of using more traditional but expensive silicon-based materials. The carbon nanotubes are excellent absorbers of sunlight, so a layer of nanotubes is used to collect the light energy as it strikes the cell. The nanotube then donates electrons to fullerene molecules. As the electrons move between the nanotube layer and the fullerene layer, an electrical charge is generated.



◀ **Figure 6.17**
A carbon-based solar cell

Nanoparticle-based solar cells

Elements such as cadmium that are used in conventional solar cell production are expensive and difficult to obtain, increasing the cost of solar cells to the consumer. Consequently, many households have not yet installed this technology.

Phosphorus and zinc are cheap and readily available but are not very useful in traditional solar cell production. However, when phosphorus and zinc are reduced to nanoparticle size, they gain new properties. Two of these properties are the ability to absorb light and increased conduction of electricity. This makes them suitable for use in solar cells. The cells produced would be cheaper and so more available to the average consumer. As they are nanoparticles, they can be applied in very thin layers. The nanoparticles pack very closely so a thin layer is sufficient to collect the amount of light needed to generate electricity.

Scientists in Canada are experimenting with spray-on solar cells using nanoparticles. They would be applied like paint to a roof or a building, connected to the electricity supply and used to generate electricity without the need for big, heavy solar cells. Technology such as this will ultimately result in more households installing solar panels, and the corresponding reduction in the use of fossil fuels will have significant positive environmental impacts.

To learn about fuel cells and how they generate electricity, refer to Chemistry section 5.5, page 264.

Fuel cells

A fuel cell converts chemical energy to electrical energy by means of a redox reaction that produces electrons. The electrons are captured and form an electric current. Fuel cells have potential to be used in large- and small-scale electricity generation because they can be big enough to power a shopping centre or large building, or small enough to run a car, or provide energy for mobile phones and laptops. As fuel cells become more efficient and portable, a reduction in the use of fossil fuel power will have significant positive environmental impacts.

Making better catalysts

Fuel cells rely on catalysts to increase the rates of reaction of the chemicals. You learnt in *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 4 that a catalyst can increase the rate of reaction by providing an alternative reaction pathway with a reduced activation energy. The faster the rate of reaction, the more electricity is produced in a given period of time.

Molecular manufacturing is producing more efficient catalysts that are being used in fuel cells. Metals such as platinum and rhodium are widely used in fuel cells for their excellent catalytic properties. These metals are rare and expensive and result in fuel cells being expensive. This makes them unaffordable for the average consumer.

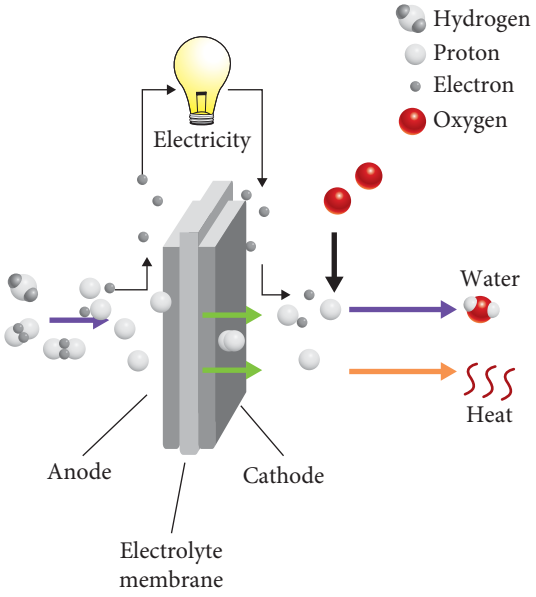
Nanopowders are being used as catalysts in fuel cells. The greater the surface area of the catalyst, the more efficient it is. Making a catalyst into a nanopowder gives a massively increased surface area for the same amount of substance. This makes the fuel cell more efficient. It is able to produce more electricity in a shorter time as the rate of the chemical reaction is increased.

Carbon nanotubes are being used as a support for traditional catalysts such as platinum. When a carbon nanotube is used with the platinum, less platinum is needed to have the same electrical output of the fuel cell. Reduced use of these expensive materials lowers the cost of a fuel cell, making it a viable alternative to fossil fuel-based electricity production.

Other examples of molecular manufactured catalysts improving the efficiency or operation of a fuel cell are:

- yttrium-stabilised zirconium nanoparticles used in a solid oxide fuel cell significantly increasing the efficiency of electricity production
- platinum–cobalt nanoparticles combined with carbon nanotubes providing a higher stable current in methanol fuel cells
- a catalyst that uses no platinum; it is made from a sheet of graphene that has a coating of cobalt nanoparticles
- a cobalt–platinum catalyst that has activity 12 times higher than platinum in its pure form. This activity was produced by controlling how the nanostructure was formed, packing the platinum in tighter than in a pure metal. This process has also been done with copper. Copper and platinum were alloyed together in nanoparticle form. The copper was then removed, which made the platinum atoms move closer together. This reduced the amount of platinum used in the fuel cell by 80 per cent.

Figure 6.18 ▼
A simplified fuel cell structure showing the membrane separating the electrodes



Fuel cell membranes

Many fuel cells use membranes to separate the anode and cathode reactions. A fuel cell membrane must let molecules and ions across the membrane so that each of the electrode reactions can occur. Chemicals or ions produced at the anode are often used by the cathode, and vice versa. The membrane allows these chemicals to cross, but not the electrons. The electrons must go through the external circuit, so they can be captured as electricity. This can be seen in Figure 6.18.

Scientists at the University of Illinois have developed a proton exchange membrane that has up to 100 times better conductivity of hydrogen ions across it than a traditional membrane. They created a silica-based nanostructure with pores about 5 nm in diameter. This traps water molecules in the pores. The water combines with acid in

the electrolyte to make an acidic solution that allows for easier passage of the hydrogen ions through the membrane.

Traditional membranes have much larger pores to allow the passage of molecules. These larger pores are not as effective at trapping the water molecules. Without the water molecules in the pores, the hydrogen ions pass between the electrodes more slowly. Improving the conduction of hydrogen ions across the membrane gives the fuel cell the ability to produce more electricity in a given time, making it more efficient.

Fuel cell materials

Fuel cells operate at a temperature range of 50–1000°C depending on the electrolyte being used. A simple hydrogen fuel cell with an acid-based electrolyte can operate at relatively low temperatures. A molten carbonate fuel cell requires very high temperatures due to the high melting points of the metal carbonate electrolyte.

Fuel cells are often limited by the temperatures that the materials inside can tolerate before melting. Nanoparticles and carbon nanotubes have been produced that have high thermal conductivity. These materials can withstand much higher temperatures than traditional materials used in fuel cells. Replacing conventional materials with nanomaterials can see an increase in the temperatures able to be used in the cell. As you learnt in *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 4, a higher temperature increases the rate of reaction, giving a fuel cell that produces more electricity in a given time.

The use of strong acids and bases in some fuel cells also causes problems when other components of the fuel cell react with these electrolytes. Many materials used in conventional fuel cells become 'poisoned' with waste chemicals such as carbon monoxide. The efficiency of the platinum catalysts often reduces after a period of time due to the reactions with waste chemicals.

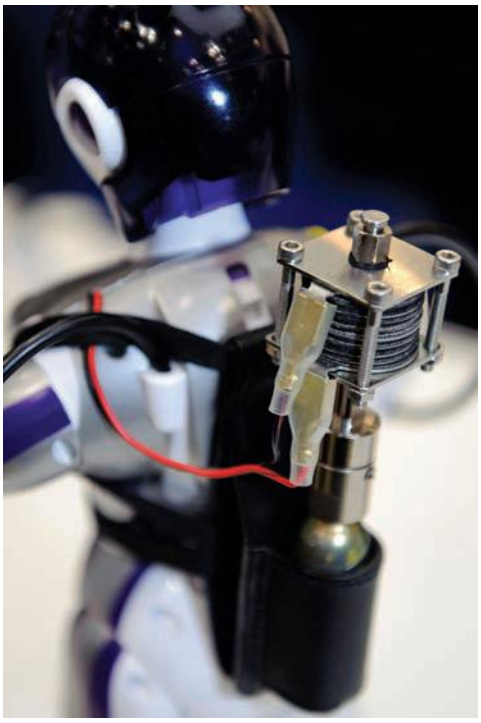
Carbon nanotubes have been used in fuel cell electrodes in place of platinum. These nanotubes do not become poisoned when carbon monoxide is formed so provide an advantage over platinum. Other nanoparticles can resist the corrosion that occurs when strongly acidic or basic chemicals are used.

WOW

Portable recharging power

As you travel from home to school or work, you probably spend time on a phone, tablet or computer. However, this often comes to an end when the battery warning appears on the screen. At this point, you look for a powerpoint to charge the device, but this is not always possible. Imagine a fuel cell you could carry around with you, about the size of a 20-cent coin, that could provide all the recharge power you wanted.

CSIRO have developed a micro fuel cell that uses methanol, a high-energy density fuel that undergoes a chemical reaction with oxygen to produce an electric current. One micro fuel cell can operate a device for six or seven times longer than a conventional lithium ion battery. The fuel cell will have a working life of 15 000 hours, or about 2 years of continuous use. And when the methanol fuel runs out, you can just change a small cartridge and go again for another 2 years!



Tony monicol/alamy

▲ **Figure 6.19**
A micro fuel cell used to power a small robot

CHAPTER SUMMARY

- Molecular manufacturing has multiple applications across medicine; for example, diagnosis of disease. Nanosensors use molecular recognition to detect the presence and level of chemicals in the body.
- Dendrimers and nanotubes are molecular manufactured structures designed to carry and deliver drugs to the site of disease in the body. They are constructed by atomic manipulation and controlled orientation of molecules to produce a specific structure. Molecular recognition and manipulation of intermolecular forces are used to deliver the structure to the correct site in the body.
- Incorporation of carbon nanotubes into clothing gives them more strength and durability than conventional fibres. Nanofibres can be produced that have different properties from the macrofibres they are developed from. The use of nanoparticles in fabrics can result in unusual materials such as fabrics that repel water and materials that can change their flexibility in response to an electrical signal.
- Atomic manipulation can produce specially designed nanocontainers that are used to hold repair materials or corrosion inhibitors. The nanocontainers respond to environmental changes to release chemicals that can cause a material to self-heal.
- Structural materials such as steel and concrete can be strengthened and made more durable by adding nanostructures. Carbon nanotubes and nanoparticles change the properties of the material through close packing of particles and providing extra strength at weak weld points.
- Molecular manufacturing has the potential to improve the production of batteries, solar cells and fuel cells, reducing dependence on fossil fuels. Batteries can use nanoparticles and nanostructures as catalysts and structural materials, making them lightweight and able to generate electricity more efficiently. Use of gels and solids as electrolytes reduces the risks associated with liquid electrolytes that are in use.
- Solar cells can be made more efficient by use of nanoparticles with better light absorption and structures that are more efficient at electron transfer. Carbon-based solar cells use the excellent electrical conductivity of carbon nanostructures to improve electron transfer and thus generate electricity more effectively. Nanoparticles of zinc and phosphorus have unique light-absorbing properties that can reduce dependence on rare and expensive conventional materials.
- Fuel cells can be made more efficient by use of nanoparticles with a high surface area that act as a more efficient catalyst than traditional platinum-type metals. Improving fuel cell components such as the proton exchange membranes and electrodes so they are not poisoned by chemicals or subject to high temperatures also increases the efficiency of a fuel cell.

CHAPTER GLOSSARY

biosensor structure that can detect a change in a biological component such as a chemical or hormone

dendrimer a molecule with a specific shape used to deliver drugs to a specific location in the body

electrospinning a process that uses the electrostatic properties of fibres to create nano-sized fibres with specific properties

fullerene an allotrope of carbon shaped like a hollow ball or cage, with specific properties such as unique electrical conduction properties

graphene an allotrope of carbon in a two-dimensional sheet that can be shaped into a variety of shapes such as nanotubes

molecular manufacturing production of chemicals with specific shapes or chemical composition

nanocontainer a nano-sized structure designed to store chemicals inside structures until the chemicals are required

nanocup a structure made from nanotubes that is shaped like a cup, designed to carry drugs inside the body

nanosensor a nano-sized structure used to detect chemicals or measure quantities of chemicals present in a particular environment

n-type semiconductor a silicon lattice structure with extra elements allowing for free electrons to move within the structure

p-type semiconductor a silicon lattice structure with elements that create space for an electron to be added to the structure

CHAPTER 1
EQUILIBRIUM



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By the end of this chapter you will have covered the following material.

Science Understanding

- Chemical systems may be open or closed and include physical changes and chemical reactions which can result in observable changes to the system (ACSCH089)
- All physical changes are reversible, whereas only some chemical reactions are reversible (ACSCH090)
- Over time, physical changes and reversible chemical reactions reach a state of dynamic equilibrium in a closed system, with the relative concentrations of products and reactants defining the position of equilibrium (ACSCH091)
- The reversibility of chemical reactions can be explained by considering the activation energies of the forward and reverse reactions (ACSCH092)
- The effect of changes of temperature on chemical systems at equilibrium can be explained by considering the enthalpy changes for the forward and reverse reactions (ACSCH093)
- The effect of changes of concentration and pressure on chemical systems at equilibrium can be explained and predicted by applying collision theory to the forward and reverse reactions (ACSCH094)
- The effects of changes of temperature, concentration of chemicals and pressure on equilibrium systems can be predicted using Le Chatelier's principle (ACSCH095)
- Equilibrium position can be predicted qualitatively using equilibrium constants (ACSCH096)



Sam Dao/Alamy

Figure C1.1 ▲
A see-saw can represent equilibrium.

1.1 Introduction

In our everyday lives there are many examples of balance or **equilibrium**. A see-saw is in equilibrium when the forces on either side are balanced and the see-saw remains horizontal. Water in a rainforest is in equilibrium when the amount of rainfall balances the amount of evaporation and use. A person's weight is in equilibrium when the amount of food eaten balances the amount used. Similarly, in chemistry some reactions achieve a balance where the amount of reactants and products remain constant, and the chemical system is in equilibrium. In each of these examples, the processes are able to go in both directions. When these processes are occurring equally, they are balanced and equilibrium is achieved.

The term 'equilibrium' always refers to a balance. However, in different contexts the exact meaning may vary. Therefore, it is important that you understand the requirements and processes for chemical equilibrium.

Collision theory

To revise collision theory and reaction rates, refer to Nelson Chemistry Units 1 & 2 for the Australian Curriculum, *Chapter 9.*

Collision theory can be used to describe what happens during a chemical reaction. It states that for a reaction to occur, the particles must collide with sufficient energy (the activation energy) and the appropriate orientation. The rate of a reaction is determined by the number of successful collisions in a given time. The greater the number of successful collisions, the faster the rate of the reaction. We can also use collision theory to understand how the rate of a reaction can be changed. This was covered in detail in Unit 2, and we will revise the key points here.

- Concentration – if the concentration of a reactant is increased, then there will be more particles in a given volume. This makes it more likely that the reactant particles will collide and so there will more collisions.
- Pressure – the pressure of a gas is due to the force exerted by the particles colliding with the walls of the container. If the pressure is increased, then there will be more particles in a given volume. Therefore, the concentration of the gaseous particles will increase and there will be more collisions between the particles. The reverse happens if the pressure is decreased.
- Temperature – if the temperature is increased, then the average kinetic energy will increase. This means that more particles will have sufficient energy for a successful collision. The increased kinetic energy is also associated with an increased speed (or velocity) of the particles, resulting in them colliding more frequently.
- Surface area – in a solid, only the exterior particles are available for a collision. Therefore, if the surface area of a fixed amount is increased, by dividing or crushing, more particles will be exposed and therefore available for a collision.
- Catalysts – catalysts interact with the reactants to provide an alternative, easier pathway for the reaction. This means that the activation energy is lower and so more particles will have sufficient energy for a successful collision.

In each of these situations, an increase in the number of successful collisions will result in an increase in the rate of the reaction.

1.2 Reversible reactions

If we put a car in reverse, we will go backwards. Therefore, the term **reversible reaction** must mean a reaction that is able to go backwards. But how is that so? Surely the reactants must form the products. They do, but sometimes the products can form the reactants.

Chemical systems

The chemicals involved in a reaction form the **chemical system**, while anything around these chemicals but not involved in the actual reaction forms the **surroundings**. For example, in the reaction between hydrogen gas and oxygen gas to form water vapour, the molecules of hydrogen, oxygen and water make up the system, while the other molecules in the air (e.g. nitrogen, carbon dioxide) form the surroundings. In an aqueous environment, the water will form part of the system if it is involved in the reaction and it will form the surroundings if it is not involved.

If the chemicals in the reaction are all contained within a certain space, the system is a **closed system**. For example, if hydrochloric acid was added to calcium carbonate in a sealed container, then nothing can enter or leave the system and it is a closed system.

Conversely, if substances can either be added or lost, then the system is described as an **open system**. For example, if hydrochloric acid is added to calcium carbonate in an open beaker, then the carbon dioxide gas produced would escape into the air. Therefore this is an open system.

When referring to an open and closed system, it is matter that can either enter or leave or not. In both situations energy is able to enter and leave the system.



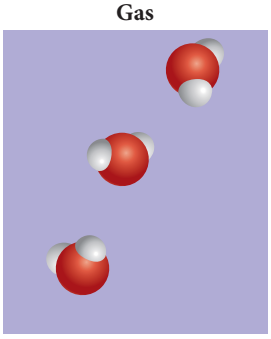
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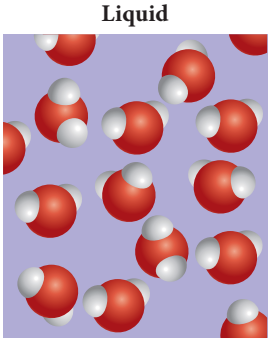
▲ **Figure C1.2**
A closed system does not allow chemicals to enter or leave.

Physical and chemical changes

The change that occurs in a chemical system can be described as a **physical change** or a **chemical change**. During a physical change, the products do not include any new substances. Instead the the physical properties of the reactant change, which can include a change of state. For example, when water is boiled, it changes from a liquid to a gas. The molecules remain the same; they are simply further apart. We can represent this change by the equation:

$$H_2O(l) \rightarrow H_2O(g)$$

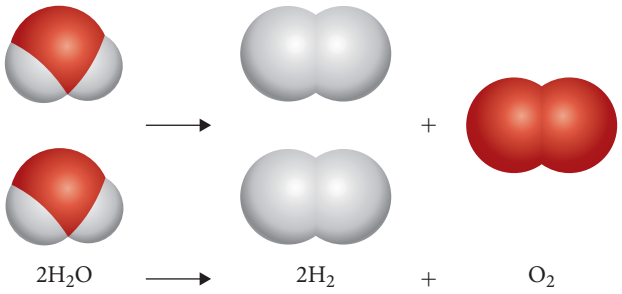




▲ **Figure C1.3**
Water boiling is a physical change.

During a chemical change, the reactants produce new substances with different physical and chemical properties from those of the original substances. For this to happen, the atoms rearrange and form products that are different from the reactants. An example of a chemical change occurs when we pass an electric current through water. The atoms in the reactant, water, rearrange to form the new substances of oxygen gas and hydrogen gas:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$



◀ **Figure C1.4**
The electrolysis of water is a chemical change.

Chemical systems may be open or closed and include physical and chemical changes, which result in observable changes.

Reversible reactions

When we think of a chemical reaction we often think of a situation where the reaction continues producing the products until one of the reactants is used up. In reality, this only happens for some reactions. In other reactions, as the products are formed some of them will react to become

To see how this applies to carbon dioxide in water, refer to Context 5, 'Aquatic chemistry', page 112.

reactants again. This means that when the reaction appears 'complete', there are both reactants and products present.

Reactions where the reactants are able to form products and the products form reactants are known as reversible reactions. All physical changes are reversible reactions. However, only some chemical changes are reversible. The reaction where the reactants form products is called the **forward reaction**, and the reaction where the products form reactants is called the **reverse reaction**.

$$CO + NO_2 \rightleftharpoons CO_2 + NO$$

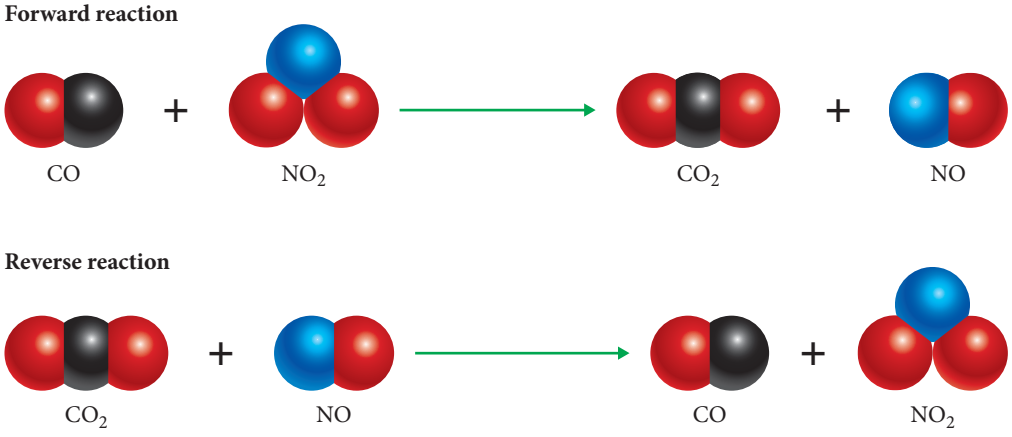


Figure C1.5 Forward and reverse reactions

The reaction between hydrogen gas and nitrogen gas is also a reversible reaction and can be represented by the following equation.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

A double arrow is used to show that the reaction can occur in both directions. In this example, hydrogen gas and nitrogen gas forming ammonia is the forward reaction. Ammonia decomposing to form hydrogen gas and nitrogen gas is the reverse reaction.

REVERSIBLE REACTIONS

Watch the video to learn more about reversible reactions.

All physical changes are reversible, whereas only some chemical reactions are reversible.

ACTIVITY 1.1

BLUE BOTTLE EXPERIMENT – A REVERSIBLE REACTION

Aim

To observe a reversible reaction

What to do

1. Watch the video on the Blue bottle weblink.
2. Alternatively, your teacher may demonstrate the reaction. The instructions may be found at the Blue bottle instructions weblink.
3. In the blue/colourless bottle, how could you tell that this was a reversible reaction?
4. In the yellow/red/green bottle, how could you tell that this was a reversible reaction?
5. What other reversible reactions have you observed?

BLUE BOTTLE EXPERIMENT

Watch this video of a reversible reaction, which is observable through colour change.

BLUE BOTTLE INSTRUCTIONS

Follow the instructions to perform the blue bottle experiment. Ensure that you follow the safety instructions.

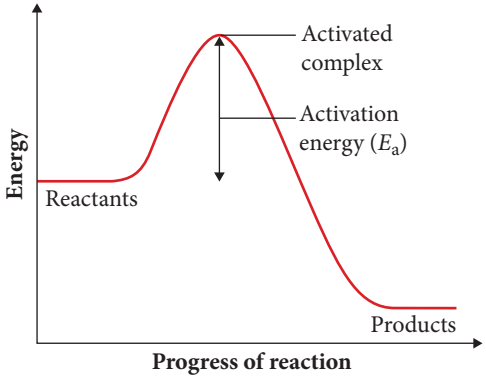
Predicting reversibility

In *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* you considered collision theory to predict the rate of reactions. Collision theory states that, for a reaction to occur, the particles must collide with sufficient energy to break the bonds and the appropriate orientation to allow the new bonds to form. This theory can also be used to understand why some reactions are reversible and others are not.

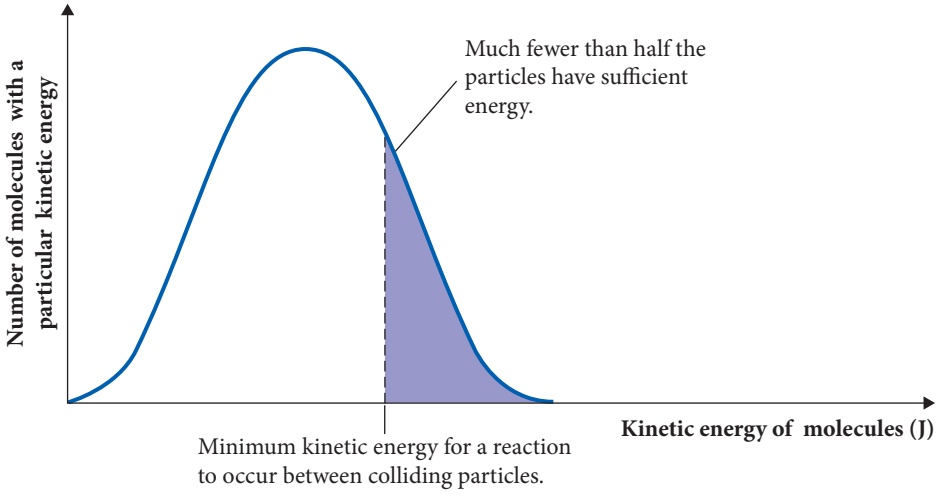
You will recall that the amount of energy required to break the bonds of the reactants is known as the **activation energy**. This is the difference in **enthalpy** between the reactants and the **activated complex**, as shown in Figure C1.6.

If the reactant particles in a collision do not have enough energy to break the bonds, then they are unable to form the products. If the activation energy is lower, then more particles will have enough energy to break the reactant bonds and form the products. Therefore, the size of the activation energy will influence the likelihood of a reaction proceeding.

In a reaction, we can consider the activation energy of both the forward and reverse reactions. If the activation energy of either of these is very high, then that reaction is unlikely to proceed because very few particles will have enough energy for a successful collision. Therefore, for a reaction to be reversible, the activation energies of both the forward and reverse reactions must be low enough that sufficient particles will have enough energy for a successful collision.



▲ **Figure C1.6**
Activation energy of a reaction



◀ **Figure C1.7**
The number of particles with enough energy for a successful collision

To revise activation energy, refer to Nelson Chemistry Units 1 & 2 for the Australian Curriculum, *Chapter 9.*

The reversibility of chemical reactions is dependent on the activation energies of both the forward and reverse reactions.

QUESTION SET 1.1

Remembering

1 State the difference between a forward and a reverse reaction.
2 State the requirements for a closed system.
3 Are all reactions reversible? Explain.

Understanding

4 Why are double arrows used in equations for reversible reactions?
5 In a particular chemical reaction, if the forward reaction is exothermic, then the reverse reaction must be endothermic. Explain the reason for this.

Applying

6 The reaction for the self-ionisation of water is an endothermic reaction:
$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
a Write the equation for the forward reaction.
b Write the equation for the reverse reaction.
c Sketch an energy profile diagram for the forward reaction.
d Sketch an energy profile diagram for the reverse reaction.

1.3 Dynamic equilibrium

In a closed chemical system involving a reversible reaction, as the reactants form products the products will also form reactants. This means that the reaction will not go to completion. Rather, it will reach a state of **dynamic equilibrium**.

Dynamic equilibrium is the state that is reached when the amount of reactants and products remains constant even though the forward and reverse reactions are still occurring.

Dynamic equilibrium is a specific example of a system in a **steady state**. Systems in steady state have constant properties. All systems at dynamic equilibrium must be in a steady state as their properties will remain constant. However, not all systems in a steady state will be in dynamic equilibrium as a steady state may be achieved without a reversible reaction or a closed system. For example, if reactants are added to a reaction mixture at the same rate that the products are removed, then a steady state will be achieved even though the system will not be at equilibrium.

Equilibrium in chemical systems

When reactants are initially placed in a system, their concentrations are high compared to the concentration of products. This means that the rate of the forward reaction is relatively high. As there are initially no products, the reverse reaction is unable to occur.

As the products form from the forward reaction, their concentration increases. This means that the reverse reaction will start to occur, and its rate will increase as the concentration of the products increases. This will occur only in a closed system where the products remain in the chemical system and so are available for the reverse reaction.

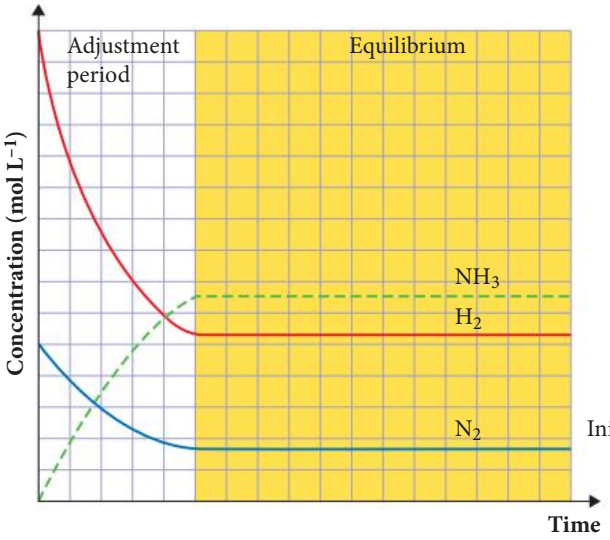
Therefore the:

- rate of the forward reaction will decrease as the concentration of the reactants decreases
- rate of the reverse reaction will increase as the concentration of the products increases.

This trend will continue until the rate of the forward reaction is the same as the rate of the reverse reaction. At this point, products are formed at the same rate that they are used up. Therefore, the concentrations of the reactants and products will remain constant. When this happens, the system is said to be in dynamic equilibrium.

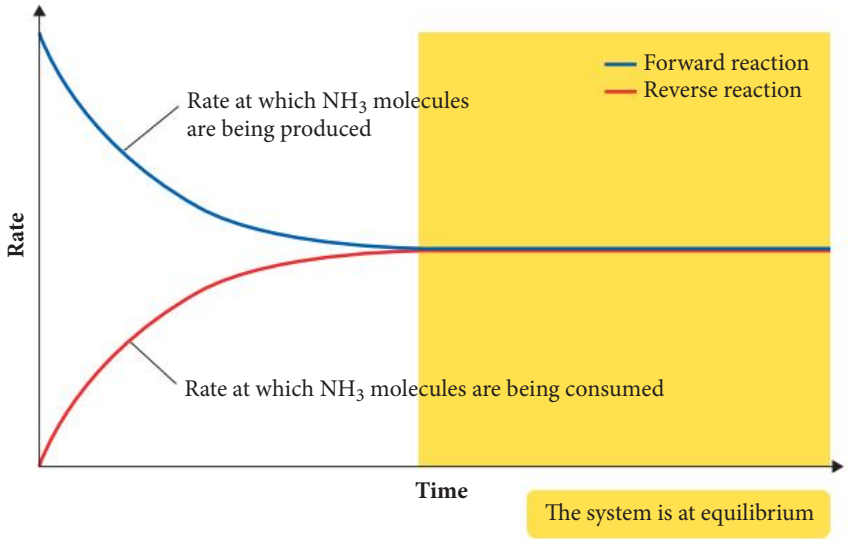
DYNAMIC EQUILIBRIUM

View the animation to observe how the forward and reverse reactions of $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ are occurring at the same rate to maintain equilibrium.



◀ **Figure C1.8**
Concentration of reactants and products vs time during the reaction:
$N_2 + 3H_2 \rightleftharpoons 2NH_3$

Initially we have N_2 and H_2 but no NH_3.



◀ **Figure C1.9**
Rate of reactions vs time for the reaction:
$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$
when H_2 and N_2 are mixed

When a system is at dynamic equilibrium, the concentrations of the reactants and products remain constant. This means that the macroscopic properties will also remain constant. For example, the colour will remain constant or the mass of a solid will stay the same. It is important to realise that although the concentrations must be constant for the system to be at equilibrium, they do not need to be equal. It is unlikely that they will be equal.

In summary, a chemical system will reach equilibrium if it:

- is a closed system
- involves a reversible reaction.

At equilibrium, the:

- rate of the forward reaction is the same as the rate of the reverse reaction
- concentrations of the reactant and products remain constant
- macroscopic properties are constant.

Reversible reactions in a closed system reach a state of dynamic equilibrium where the concentrations of reactants and products remain constant.



Figure C1.10 ▲
A system at dynamic equilibrium will maintain constant macroscopic properties.

Graphing and equilibrium

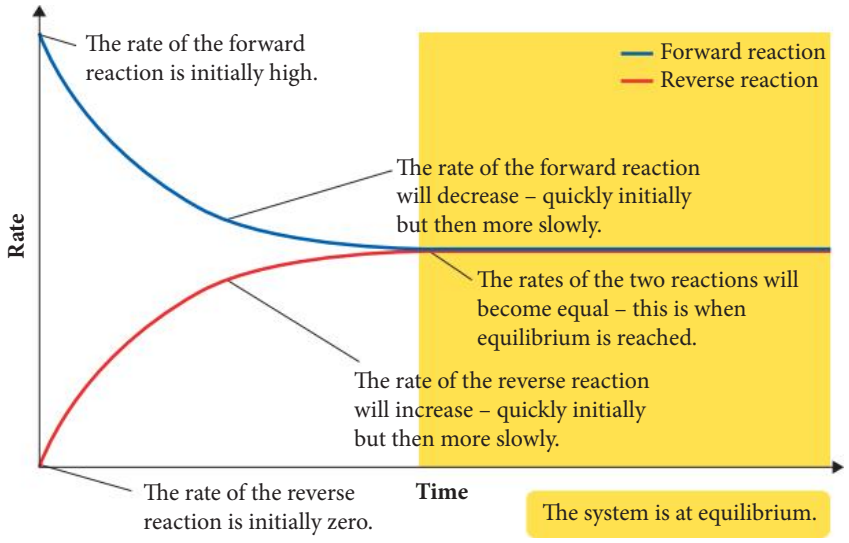
Graphing is used in many situations to visually represent data. When you are studying chemical systems involving equilibrium, you can use graphs to consider either the rates of the reactions or the concentrations of the substances over time.

Graphing reaction rate and time

In a graph of reaction rate versus time, when we start with reactants only, you will observe that the rate of the:

1 forward reaction is initially high
2 reverse reaction is initially zero
3 forward reaction will decrease – quickly initially but then more slowly
4 reverse reaction will increase – quickly initially but then more slowly
5 two reactions will become equal – this is when equilibrium is reached.

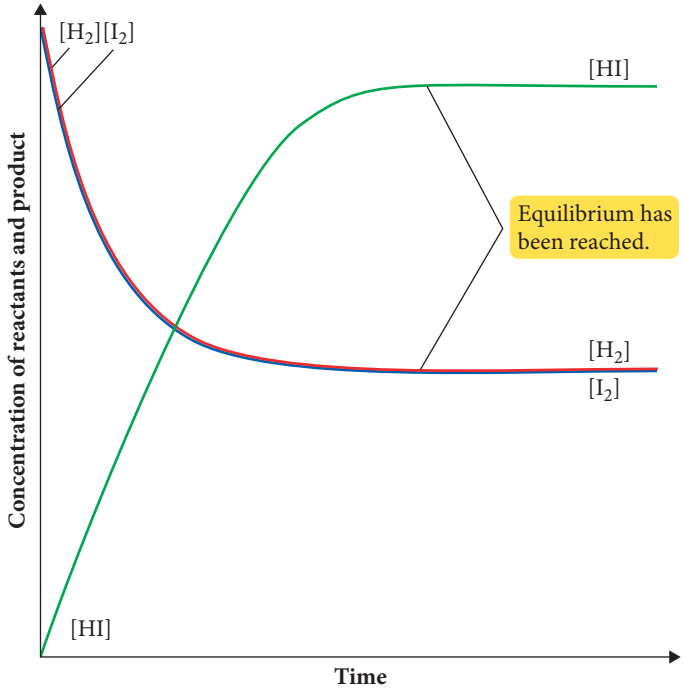
Figure C1.11 ▶
Reaction rate vs time for the reaction:
$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$



Graphing concentration and time

Similarly, you can use a graph to represent the changes in concentration during a reaction as it reaches equilibrium. Typically, the reaction will start with only reactants; therefore, the concentration(s) of:

1 reactants is initially large
2 products is initially zero
3 reactants decreases, initially quickly (steep graph) and then more slowly
4 products increase, initially quickly (steep graph) and then more slowly
5 all will plateau when the system reaches equilibrium.



◀ **Figure C1.12**
Concentration vs time for the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Table C1.1 Graphing concentration and reaction rate vs time

Graph	Number of lines	Position of line at equilibrium
Concentration vs time	Any number depending on the number of reactants and products. Each may be represented on the graph by a separate line	All lines plateau as concentrations are constant. They do not need to be of equal value.
Reaction rates vs time	Two lines – forward reaction and reverse reaction	The two lines meet and plateau as the two rates are equal.

Equilibrium constant

Just like a see-saw at equilibrium, a chemical system at equilibrium has a balance between the reactants and products. However, unlike the see-saw example, in a chemical system the amounts do not need to be equal. Rather, there is a mathematical relationship between the concentrations of the reactants and products. This relationship is known as the **equilibrium constant** or ***K***.

The equilibrium constant is specific for a particular reaction at a particular temperature. It can be calculated from the concentrations of the reactants and products at equilibrium in the **equilibrium expression**.

For the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium expression is:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

As the equilibrium expression is determined from the way the equation is written, the magnitude of K will also depend on the equation.

ACTIVITY 1.2

CALCULATING THE EQUILIBRIUM CONSTANT

Aim

To develop an understanding of the equilibrium constant

What to do

Complete each question in order.

1 Consider the reaction where dinitrogen tetraoxide forms nitrogen dioxide:

$N_2O_4 \rightleftharpoons 2NO_2$

At equilibrium, the following concentrations were recorded. Remember that square brackets indicate molar concentration.

a Copy and complete the table.

Trial	$[N_2O_4]$ $(mol\,L^{-1})$	$[NO_2]$ $(mol\,L^{-1})$	$[N_2O_4]^2$	$[NO_2]^2$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$	$\frac{[NO_2]}{[N_2O_4]^2}$
1	3.476	1.048					
2	2.56	0.899					
3	0.830	0.512					
4	1.95	0.785					
5	0.0123	0.0623					

b What do you notice about the values in each column?

c Can you see any relationship between the pattern and the equation?

2 Consider the reaction:

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

a Copy and complete the table using the equilibrium concentrations listed.

Trial	$[PCl_5]$ $(mol\,L^{-1})$	$[PCl_3]$ $(mol\,L^{-1})$	$[Cl_2]$ $(mol\,L^{-1})$	$\frac{[PCl_5]}{[PCl_3][Cl_2]}$	$\frac{[PCl_3][Cl_2]}{[PCl_5]}$
1	2.30	0.971	0.971		
2	0.62	1.69	0.15		
3	1.05	0.41	1.05		
4	0.0292	3.75	3.75		
5	5.90	1.56	1.55		

b What do you notice about the values in each column?

c Can you see any relationship between the pattern and the equation?

3 Consider the reaction between hydrogen and iodine producing hydrogen iodide:

$H_2 + I_2 \rightleftharpoons 2HI$

a Reflect on the patterns you have seen in the first two questions to predict the relationship that will exist in this reaction.

b Use the equilibrium concentrations below to test your hypothesis.

Trial	$[H_2]$ $(mol\,L^{-1})$	$[I_2]$ $(mol\,L^{-1})$	$[HI]$ $(mol\,L^{-1})$
1	2.5	2.5	17.7
2	0.226	0.226	1.6
3	1.25	3.00	13.7
4	0.015	0.020	0.122

c Were you correct?

4 Summarise your findings for calculating the equilibrium constant by referring to the following general equation:

$aA + bB \rightleftharpoons cC + dD$

What is included in the equilibrium expression?

The equilibrium constant is based on the ratio of the concentration of reactants and products. Solutions vary in concentration and therefore are included in the equilibrium expression. Gases also vary in concentration and are included. The partial pressure (the pressure of the individual gas) is proportional to the concentration of the gas and therefore can also be used in the equilibrium expression for a gaseous system.

However, solids and liquids do not vary in their concentration. Therefore, in a heterogeneous system where the substances are in more than one phase, solids and liquids are not included in the equilibrium expression. In a homogeneous system, where all substances are in the same phase, solids and liquids are included because the relative proportions are important.

Why temperature affects the equilibrium constant

In Year 11, you learnt how the temperature of a system will affect the proportion of particles with enough energy to overcome the activation energy and therefore react to become products. In reversible reactions, both the forward and reverse reactions have activation energies. A change in temperature will change the proportion of particles with enough energy for each reaction to proceed. The extent of these changes relative to each other will determine the relative amount of products and reactions, and therefore the equilibrium constant.

WORKED EXAMPLE 1.1

a Write the equilibrium expression for $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

b Write the equilibrium expression for $CaCl_2(s) \rightleftharpoons Ca^{2+}(aq) + 2Cl^-(aq)$

Answer

a $K = \dfrac{[NH_3]^2}{[H_2]^3[N_2]}$

Logic

1. Put the products on top of the expression; reactants underneath.
2. Add square brackets around each substance to indicate concentration.
3. The coefficient for each species from the equation becomes the power in the expression.
4. Multiply concentrations if there is more than one reactant or product.

b $K = [Ca^{2+}][Cl^-]^2$

1. Put the products on top, reactants on bottom.
2. Add square brackets around each substance to indicate concentration.
3. The coefficient for each species from the equation becomes the power in the expression.
4. Multiply concentrations if there is more than one reactant or product.
5. Exclude solids and liquids in heterogeneous equilibria.

Try these yourself

Write the equilibrium expression for each of the following reactions.

a $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

b $H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$

c $CaCO_3(s) \rightleftharpoons CaO(s) + O_2(g)$

d $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$

e $2CrO_4^-(aq) + 2H^+ \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$

Reaction quotient (*Q*)

The ratio of products to reactants $\dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ will only equal the equilibrium constant (K) when the system is at equilibrium. The reaction quotient (Q) is also calculated from the same ratio. If $Q = K$, then the system is at equilibrium. If $Q < K$, then there are less products and more reactants than at equilibrium. This indicates that the forward reaction will be favoured for the system to reach equilibrium. Conversely, if $Q > K$, then there are more products and less reactants than at equilibrium. This indicates that the reverse reaction will be favoured for the system to reach equilibrium.

Although the reaction quotient is not studied in the Australian Curriculum for Chemistry, it provides another way of viewing chemical equilibrium – a more mathematical viewpoint. You may wish to research this yourself, with your teacher or during further studies.

Size of the equilibrium constant

The magnitude of K can tell us whether there are more products or reactants at equilibrium. As the products are on top of the fraction, a large value of K indicates the concentration of products is much greater than the concentration of reactants. Therefore, a:

- large value of K indicates that the reaction goes towards completion, meaning that nearly all of the reactants become products. We say that equilibrium lies to the right, as there are more products present at equilibrium than reactants

- small value of K indicates that the reaction only occurs to a small extent. We say that equilibrium lies to the left, as there are more reactants than products at equilibrium
- value of K close to 1 indicates that there are significant concentrations of both reactants and products present at equilibrium.

For example, the equilibrium constant for the pop test, which is the reaction between hydrogen and oxygen gas to form water vapour, is 2.4×10^{47} at 500 K.

The equation for this reaction is:

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

Therefore, the equilibrium expression is:

$$K = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

The very high value of the equilibrium constant shows that, at equilibrium, there is a large amount of products (H_2O) and only a very small amount of reactants (H_2 and O_2). This indicates that most of the reactants react to become products, so the reaction occurs to a large extent. In this case, we say that the position of equilibrium is to the right.

Alternatively, the reaction for hydrogen molecules splitting into hydrogen atoms has an equilibrium constant of 1.2×10^{-42} at 500 K.

$$H_2(g) \rightleftharpoons 2H(g)$$

$$K = \frac{[H]^2}{[H_2]}$$

The very low value for the equilibrium constant indicates that, at equilibrium, there is a large proportion of the reactant, H_2 molecules, compared to the product, H atoms. This shows that the reaction only occurs to a very small extent. In this case, we say that the position of equilibrium is to the left.



To see an example of equilibrium, refer to Context 1, 'Wine', page 15, and Context 5, 'Aquatic chemistry', page 117.

Equilibrium constants predict the relative concentrations of products and reactants and therefore the position of equilibrium.

WORKED EXAMPLE 1.2

Calculate the magnitude of the equilibrium constant for the reaction:

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

given that, at equilibrium, $[CH_3COOH] = 0.92\ mol L^{-1}$, $[CH_3COO^-] = 1.62 \times 10^{-2} mol L^{-1}$ and $[H^+] = 1.02 \times 10^{-3} mol L^{-1}$.

Answer

$K = 1.8 \times 10^{-5}$

Logic

1 Write the equilibrium expression.

$$K = \frac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]}$$

2 Substitute the given concentrations into the expression.

$$K = \frac{(1.62 \times 10^{-2}) \times (1.02 \times 10^{-3})}{0.92}$$

3 Calculate the answer.

$K = 1.8 \times 10^{-5}$

Try these yourself

Calculate the magnitude of the equilibrium constant for each of the following examples.

a $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$, given that $[CO_2] = 2.00 mol L^{-1}$, $[H_2] = 3.00 mol L^{-1}$, $[CO] = [H_2O] = 0.17 mol L^{-1}$.

b $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$, given that $[H_2S] = 0.2 mol L^{-1}$, $[H_2] = 7.0 \times 10^{-3}$ and $[S_2] = 3.5 \times 10^{-3}$.



To see how conditions are manipulated to improve yield, refer to Context 2, 'Chemical industry', page 49.

Yield and rate

The **yield** and rate are two different aspects of a reaction. The yields refers to how much product can be produced. This is dependent on the position of equilibrium and therefore the magnitude of the equilibrium constant. A high value of K indicates a high yield. The rate refers to how quickly this yield will be achieved.

QUESTION SET 1.2

Remembering

1 State the requirements for dynamic equilibrium.

2 Define equilibrium constant.

3 What is the only characteristic that will change the magnitude of the equilibrium constant for a reaction?

Understanding

4 Explain the difference between steady state and dynamic equilibrium.

Applying

5 Write the equilibrium expression for:

a $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

b $H_2O(l) + HSO_4^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$

6 Equal moles of PCl_3 and Cl_2 are placed in a closed container and react until they reach equilibrium according to the equation below.

$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

Sketch a graph showing the relative concentrations of all species in the system.

Analysing

7 The equilibrium constant for $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ is 14.5 at 483 K. If the concentration of CO and H_2 are both 0.5 mol L^{-1} and the concentration of CH_3OH is 5 mol L^{-1}, is the system at equilibrium?

1.4 Changes to equilibrium

When equilibrium is established in a chemical system, it depends on the conditions of the system. By understanding what happens during a reaction, we can explain the changes in equilibrium when these conditions are altered. This also allows us to choose conditions that best suit the purpose of the reaction.

If the temperature, concentration or **partial pressure** of chemicals or volume of a system is changed, the ratio of products to reactants is no longer the same as the equilibrium constant. This indicates that the system is no longer at equilibrium. Either the forward or reverse reaction is favoured as equilibrium is re-established. This will change the concentrations, so their ratios equal the equilibrium constant.

If the forward reaction is favoured, then we say that equilibrium has shifted to the right. This is as more products will be produced, and products lie on the right-hand side of the equation. Conversely, if the reverse reaction is favoured, then equilibrium shifts to the left due to the production of more reactants. Note: This does not mean that equilibrium literally sits on the left or right. These are simply expressions comparing the relative concentrations at equilibrium before and after a change.

Changes to concentration and partial pressure

To see how equilibrium in aqueous environments is affected by change, refer to Context 5, 'Aquatic chemistry', page 118.

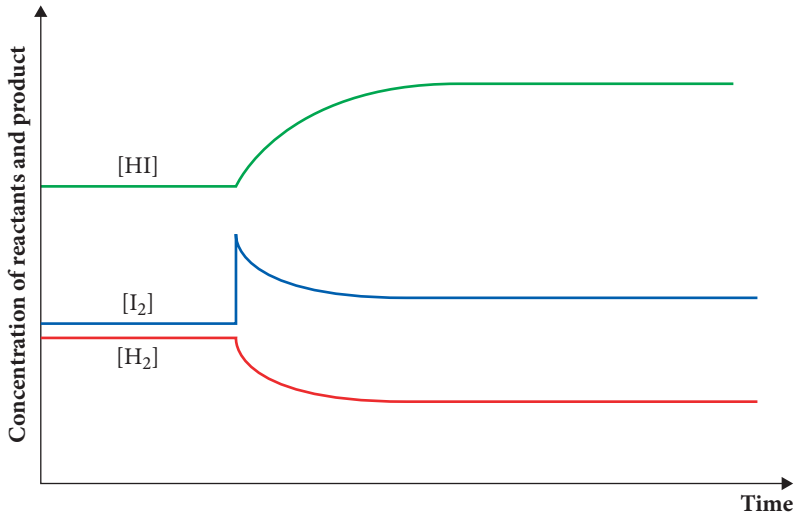
From our understanding of collision theory and reaction rates, we know that an increase in the concentration of a reactant will increase the rate of the reaction due to the increased number of collisions. In reversible reactions, if the concentration of a reactant is increased, then the rate of the forward reaction will increase. Alternatively, if the concentration of a product is increased, then the rate of the reverse reaction will increase.

If the concentration of one chemical in a system at equilibrium is increased, then the rate of the reaction that uses that chemical will increase. This will use up some of the additional chemical, reducing the concentration, and therefore this rate will gradually decrease. At the same time, the rate of the opposite reaction will increase as more of its reactants are produced. Eventually the rates of the two reactions will once again become equal, and equilibrium is re-established.

Consider the reaction between hydrogen and iodine to form hydrogen iodide:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

If more iodine is added to the system, then the concentration of the iodine is increased. As the iodine is a reactant for the forward reaction, the rate of the forward reaction will increase. This means that the concentration of hydrogen gas and iodine will decrease while the concentration of the hydrogen iodide will increase. As more hydrogen iodide is produced, the rate of the reverse reaction will begin to increase. This pattern will continue until the rates of the forward and reverse reactions are once again equal. At this time, the concentrations of each chemical will remain constant. The new concentration of iodine will be lower than the concentration following the addition of the extra iodine. However, it will not return to the original concentration.



◀ **Figure C1.13**
Concentrations following a change in concentration for the reaction:
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

The partial pressure of a gas and its concentration are related because they are both due to the number of particles in a given volume. Therefore, a change in partial pressure will cause a proportional change in concentration. This means that in a gaseous system, the partial pressures of the gases can be used to indicate the concentration.

The same logic can be applied to a decrease in concentration. A decrease in concentration will lead to a decrease in the rate of the reaction that uses that substance. Over time, the concentration of the reactants for that reaction will increase as less are used up while the concentration of the products for that reaction will decrease. However, the concentration of the substance that was removed will not return to the original concentration.

CHANGES TO CONCENTRATION

View the animation to see how a change in concentration button affects a reaction.

The effects of changes of concentration of chemicals can be explained by applying collision theory.

EXPERIMENT 1.1

EFFECT OF CHANGES TO CONCENTRATION ON EQUILIBRIUM

In an aqueous solution of chromate or dichromate salts, an equilibrium will exist between the two ions:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

The chromate ion is yellow whereas the dichromate ion is orange. Therefore, the colour of the solution will indicate the relative proportions of the two ions, and hence the position of equilibrium. If the solution is a yellow colour, then there are more chromate ions than dichromate ions and the equilibrium lies more to the left. Alternatively, if the solution is orange, there are more dichromate ions than chromate ions and equilibrium lies to the right.

Aim

To observe the effect of a change in concentration on a system at equilibrium

Materials

- 5 mL of 0.1 mol L^{-1} potassium chromate (K_2CrO_4)
- 5 mL of 0.1 mol L^{-1} potassium dichromate ($K_2Cr_2O_7$)
- 5 mL of 0.2 mol L^{-1} sodium hydroxide (NaOH)
- 5 mL of 0.2 mol L^{-1} hydrochloric acid (HCl)
- Distilled water
- 4 test tubes
- 10 mL measuring cylinder

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
0.2 mol L^{-1} HCl is corrosive to skin and clothing.	Wear gloves, safety glasses and an apron.
0.2 mol L^{-1} NaOH may cause irritation to eyes and skin.	Wear gloves, safety glasses and an apron.
Potassium dichromate and potassium chromate are oxidising agents and may cause cancer and respiratory allergic reactions.	Handle with care. Wear gloves, safety glasses and an apron. Keep away from combustible materials. Do not dispose of these chemicals down the sink.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Place approximately 1 mL of 0.1 mol L^{-1} potassium chromate into a test tube. Observe the colour and keep this test tube as a reference for the colour of the chromate ion.
2. Place approximately 1 mL of 0.1 mol L^{-1} potassium dichromate into a test tube. Observe the colour and keep this test tube as a reference for the colour of the dichromate ion.
3. Place approximately 1 mL of 0.1 mol L^{-1} potassium chromate into a clean test tube. Add 0.2 mol L^{-1} hydrochloric acid to the solution drop by drop until a colour change is observed. Compare this colour with your reference test tubes.
4. To the same test tube used in step 3 add 0.2 mol L^{-1} sodium hydroxide drop by drop until a colour change is observed. Compare this colour with your reference test tubes.
5. Place approximately 1 mL of 0.1 mol L^{-1} potassium dichromate into a clean test tube. Add 0.2 mol L^{-1} sodium hydroxide to the solution drop by drop until a colour change is observed. Compare this colour with your reference test tubes.
6. To the same test tube used in step 5 add 0.2 mol L^{-1} hydrochloric acid drop by drop until a colour change is observed. Compare this colour with your reference test tubes.
7. Follow your teacher's instructions for the disposal of the chemicals.

Results

Present your observations in a simple table.

Analysis of results

1 a What happened to the colour of the chromate solution when the hydrochloric acid was added?
  b Why did this happen?
2 a What happened to the concentration of hydrogen ions when the sodium hydroxide was added to the chromate solution in step 4?
  b Write an equation to demonstrate this reaction.
  c What colour change was observed in step 4?
  d Why did this happen?
3 Account for the colour change observed in steps 5 and 6.

Discussion

1 Compare the colours observed in steps 3–6 to the reference test tubes. Suggest a reason for any differences that occurred.
2 The volumes used in this experiment were approximate volumes. Did this affect the results? Explain your answer.

Conclusion

1 What conclusion can you make regarding the shift in equilibrium following:
  a an increase in concentration of a reactant or product?
  b a decrease in concentration of a reactant or product?

Changes to volume and pressure

When the volume or pressure of a gaseous system is changed, the concentrations of all gaseous substances are altered. This means that the concentration of both reactants and products may change. Whichever one changes the most will have the greatest influence on the change on equilibrium.

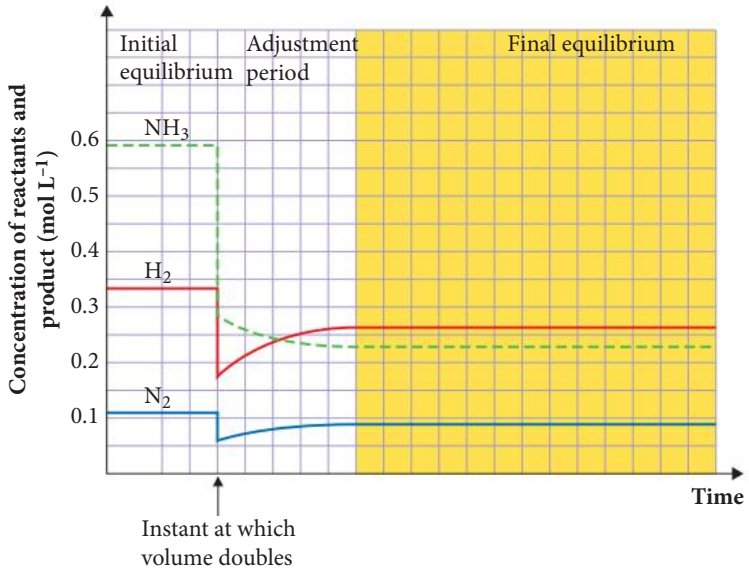
If you consider the reaction between nitrogen gas and hydrogen gas producing ammonia, then you can see that there is a 4:2 ratio of gas molecules between the reactants and products −3 molecules of H_2 and 1 molecule of N_2 are used for every 2 molecules of NH_3 produced:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

If the volume of the system was halved, then the pressure, and therefore concentration, of all the gases would double. The rate of both the forward and reverse reactions would therefore increase. There is a greater proportion of gas molecules in the reactants and so the rate of the forward reaction will increase more than the reverse reaction. As the reactions proceed, the concentrations of hydrogen and nitrogen will decrease and the concentration of ammonia will increase. Similarly the rate of the forward reaction will decrease and the rate of the reverse reaction will increase until the two are once again equal and equilibrium is re-established. The opposite will happen if the volume of a gaseous system is increased.

CHANGES TO THE VOLUME OF A GASEOUS SYSTEM

Visit this website to see a graph that shows the relative number of moles of substances involved in the reaction: $C(s) + H_2O(l) \rightarrow CO(g) + H_2(g)$.



◀ Figure C1.14
Changing the volume of a gaseous system

If the volume of a solution is changed by adding or removing water, then the same principle will apply as the concentration of all aqueous substances will change. For example, if water is added to the solution, then the concentration of all aqueous components will decrease. The rate of the reaction that uses the greater proportion of aqueous molecules will initially decrease the most. The rate of this reaction will then gradually increase while the rate of the opposite reaction will decrease until the two are once again equal and equilibrium is re-established.

The effect of a change in volume or pressure of a chemical system can be explained by applying collision theory.

Another situation to consider is where there are equal number of molecules of gases (or aqueous) molecules in the reactants and products of the equation. This means that if the volume is changed, then the concentration of reactants and products change equally and therefore the rates of both the forward and reverse reactions also change equally and remain equal. Therefore equilibrium has not been altered.

For example, in the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, there are 2 molecules of gas in the reactants ($1 \times H_2$ and $1 \times I_2$) and 2 molecules of gas in the products ($2 \times HI$). Therefore, there is an equal number of moles of gas on both sides. A change in the volume of the container would not affect equilibrium.

EXPERIMENT 1.2

CHANGING THE VOLUME OF A GASEOUS SYSTEM AT EQUILIBRIUM

An equilibrium exists between the gases nitrogen dioxide and dinitrogen tetraoxide:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Nitrogen dioxide is a brown gas, while nitrogen tetraoxide is colourless. This means the colour can indicate the proportion of gases in the mixture. A darker brown indicates a greater concentration of nitrogen dioxide and therefore an equilibrium that lies further to the left. Conversely, a lighter brown colour indicates a lower concentration of nitrogen dioxide and therefore an equilibrium lies further to the right.

Aim

To observe the effect of changing the volume of a gaseous system at equilibrium

Materials

- Large, transparent syringe containing NO_2/N_2O_4

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
NO_2/N_2O_4 is hazardous if inhaled or comes in to contact with skin, eyes or mucous membranes.	Ensure the syringe is sealed. Conduct experiment in a fume hood.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Your teacher will demonstrate this experiment.
2. Observe the colour of the gas mixture in the syringe.
3. Quickly push in the plunger of the syringe to reduce the volume. Observe the immediate change in the colour of the gas mixture and then the changes that occur over the next few seconds as equilibrium is re-established.

Results

Record your observations in a simple table.

Analysis of results

1 What happened to the intensity of the colour when the volume was initially reduced? Why did this occur?

2 What happened to the intensity of the colour as equilibrium was re-established? Why did this occur?

Discussion

1 Use your knowledge of collision theory to account for the changes that were observed.

2 Predict the changes that would be observed if the volume of the system was increased. Your teacher may demonstrate this for you so that you can see whether your prediction is correct.

3 What factors would affect the change observed in a gaseous system when the volume is altered?

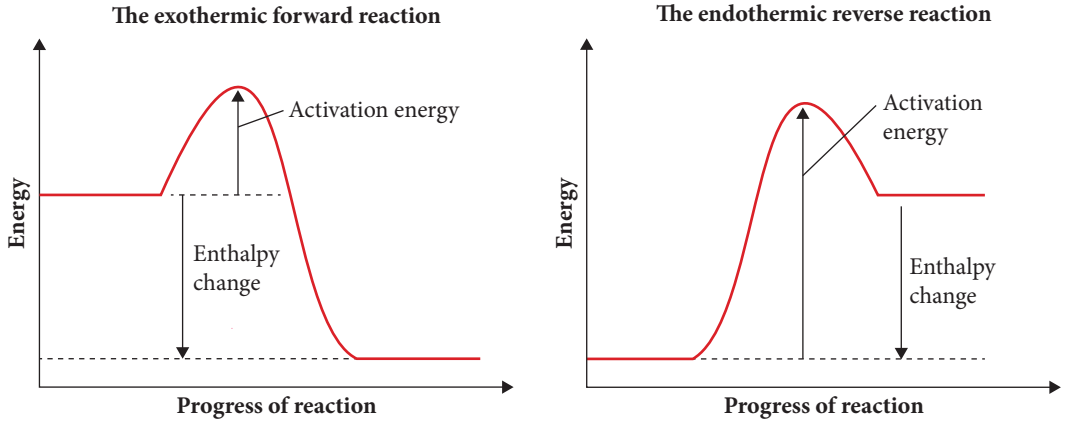
Conclusion

What conclusion can you make about the changes that are observed when the volume is changed in a gaseous system?

Changes to temperature

You have previously learnt that a change in temperature will lead to a change in the equilibrium constant for that reaction. This means that the ratio of reactants to products at equilibrium will depend on the temperature.

Remember that in an **endothermic reaction**, the products have more enthalpy than the reactants, meaning that energy will be absorbed from the surroundings. Alternatively, in an **exothermic reaction**, the reactants have more enthalpy than the products and therefore energy will be released to the surroundings. In a reversible reaction, the reaction in one direction will be endothermic while the reaction in the opposite direction will be exothermic. In both reactions, the activation energy is the difference between the enthalpy of the activated complex and the reactants. The lower enthalpy of the reactants in the endothermic reaction means that the endothermic reaction will have a greater activation energy than the exothermic reaction for the same reversible reaction.



▲ Figure C1.15 Comparing the activation energy for the forward and reverse reactions of: reactants $\rightleftharpoons$ products + energy
Note how the activation energy for the endothermic reaction is greater than the activation energy for the exothermic reaction.

To revise the effect of temperature on the rate of reactions, refer to Nelson Chemistry Units 1 & 2 for the Australian Curriculum, *Chapter 9.*

When the temperature of a system is increased, the rate of both the forward and reverse reactions will increase. However, the rate of the endothermic reaction will increase more. This is because due to the higher activation energy, the increase in temperature will affect the percentage of particles able to react in the endothermic reaction more than in the exothermic reaction. As more of the products of the endothermic reaction are produced, the opposite, exothermic reaction rate will increase. At the same time, the rate of the endothermic reaction will decrease as these reactants are used up. This trend will continue until the two rates are once again equal and the system is at equilibrium. It should be noted that while the rates description describes how equilibrium is achieved, it is not the rate that drives the equilibrium change.

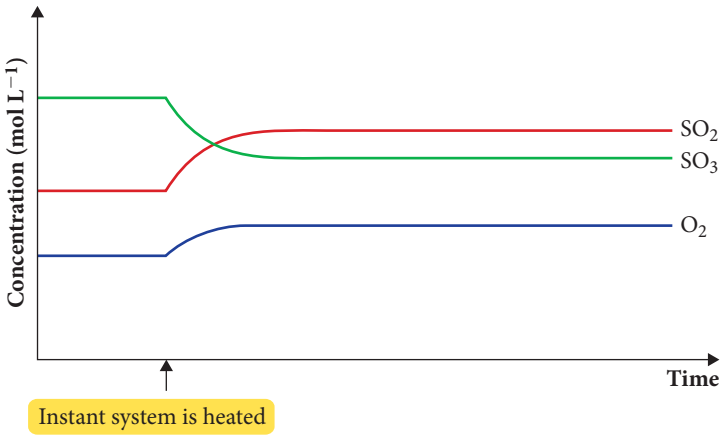
The effect of temperature changes on a chemical system can be explained by considering the enthalpy changes for the forward and the reverse reactions.

The reaction between sulfur dioxide and oxygen to produce sulfur trioxide is an exothermic reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -197\,kJ\,mol^{-1}$$

This means that the forward reaction is exothermic while the reverse reaction is endothermic. If the temperature of the system is increased, then the endothermic reaction will be favoured. This will result in an increase in the concentrations of $SO_2(g)$ and $O_2(g)$ and a decrease in the concentration of $SO_3(g)$. Therefore, K at the higher temperature will be lower than K at the original temperature for this reaction.

Figure C1.16 ▶ Concentrations with a change in temperature for the reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$



The opposite trend occurs when the temperature decreases. The rate of both the forward and reverse reactions will decrease. However, the rate of the endothermic reaction will decrease more, meaning that the rate of the exothermic reaction will be faster. Over time, the rate of the endothermic reaction will increase while the rate of the exothermic reaction will decrease until the two are equal again and equilibrium is re-established.

Consider the reaction system at equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = +57\,kJ\,mol^{-1}$$

If the temperature of the system was decreased, the exothermic reaction would be favoured. This would result in an increased concentration of N_2O_4 and a decreased concentration of NO_2. Therefore, the magnitude of K at the reduced temperature would be lower than at the original temperature.

In summary, a change in temperature will result in a shift in equilibrium that will affect the equilibrium constant (Table C1.2). If the change in temperature favours the forward reaction, then there will be an increase in the concentration of products and a decrease in the concentration of the reactants. Therefore, the magnitude of the equilibrium constant will increase. Alternatively, if the reverse reaction is favoured, then there will be an increase in the concentration of the reactants and a decrease in the concentration of products. This will decrease the magnitude of the equilibrium constant.

Table C1.2 The effect of a change in temperature on the equilibrium constant

Change in temperature	Forward reaction	Reverse reaction	Favoured reaction	Equilibrium constant
Increase	Exothermic	Endothermic	Endothermic/ reverse	Decrease
	Endothermic	Exothermic	Endothermic/ forward	Increase
Decrease	Exothermic	Endothermic	Exothermic/ forward	Increase
	Endothermic	Exothermic	Exothermic/ reverse	Decrease

Addition of a catalyst

The addition of a catalyst does not affect equilibrium. However, it does affect how quickly equilibrium is attained. A catalyst will decrease the activation energy of both the forward and reverse reactions equally. The rates of both the reactions will increase; however, they remain the same. This is why equilibrium is not disturbed.

EXPERIMENT 1.3

EFFECT OF TEMPERATURE ON A SYSTEM AT EQUILIBRIUM

An equilibrium will exist between $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ when they are in a solution. The equation representing this is:

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

The $[Co(H_2O)_6]^{2+}$ ion is a pink colour while the $[CoCl_4]^{2-}$ ion is a deep blue colour. Therefore, the relative concentrations of the ions and therefore the position of equilibrium will be indicated by the colour of the solution. A blue solution indicates a high concentration of $[CoCl_4]^{2-}$ compared to $[Co(H_2O)_6]^{2+}$. Alternatively, a pink solution indicates a high concentration of $[CoCl_4]^{2-}$ compared to $[Co(H_2O)_6]^{2+}$.

Aim

To observe the effect of changing the temperature of a system at equilibrium

Materials

- 3 g cobalt(II) chloride-6-water $[CoCl_2.6H_2O]$
- Distilled water
- 5 mL of concentrated hydrochloric acid
- 3 large test tubes
- Bunsen burner
- Test tube tongs
- Heat mat

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Concentrated HCl is very corrosive to skin and clothes.	Wear gloves and an apron. If any acid comes in contact with skin, wash it immediately with plenty of water.
Cobalt(II) chloride-6-water may be an irritant to eyes, skin and respiratory systems. It may cause cancer.	Use in a well-ventilated area. Wear gloves, safety glasses and an apron. If any comes in contact with skin, wash it immediately with plenty of water.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Dissolve a pea-sized amount of $CoCl_2.6H_2O$ in 1–2 mL of distilled water in a test tube. Observe and record the colour of the resultant solution. This colour is due to the $[Co(H_2O)_6]^{2+}$ ion. Keep this test tube as a reference.
2. Dissolve a pea-sized amount of $CoCl_2.6H_2O$ in 1–2 mL of concentrated hydrochloric acid in a clean test tube. Observe and record the colour of the resultant solution. This colour is due to the $[CoCl_4]^{2-}$ ion. Keep this test tube as a reference.
3. Dissolve a pea-sized amount of $CoCl_2.6H_2O$ in 1–2 mL of distilled water in the third test tube. Gently heat the solution over the Bunsen burner until the solution is almost boiling. Observe and record the colour change.
4. Allow the third test tube to cool down, observing and recording the colour change.

Results

Record your results in a simple table.

Analysis of results

1. What colour change was observed when the test tube was heated? What does this colour indicate regarding the relative proportion of the two ions?
2. What colour change was observed when the test tube cooled down? What does this colour indicate regarding the relative proportion of the two ions?

Discussion

1. Which reaction was favoured when the test tube was heated?
2. Is the forward reaction exothermic or endothermic? Explain your answer.
3. How would the equilibrium constant for this reaction change with an increase in temperature? Explain your answer.
4. What other factors may have contributed to the observations?

Conclusion

What conclusion can you make regarding the effect of temperature on the equilibrium between $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$?

Le Chatelier's principle

Henri Louis Le Chatelier summarised the trends involved in a change in the conditions of a system at equilibrium in **Le Chatelier's principle**. This principle can be used to predict the changes that will occur following a change in concentration of chemicals, pressure, volume or temperature of a system.

Le Chatelier's principle states that:
If a system at equilibrium is subject to a change in conditions, then the system will behave in such a way so as to partially counteract the change.

To use Le Chatelier's principle to predict the outcome of a change in conditions we need to consider:

1 What is the change imposed?
2 What is the opposite of the change? This is what the system will do.
3 Which reaction is favoured – the forward or reverse?
4 Does equilibrium shift to the left or right?
5 What happens to the concentrations of each aqueous substance or gas?



To see how Le Chatelier's principle is applied to an aquatic system, refer to Context 5, 'Aquatic chemistry', page 119.

Changes to concentration or partial pressure

According to Le Chatelier's principle, when the concentration of a substance involved in a reaction is altered, the system will react to counteract the change and return the concentration towards its original level.

This means that if the concentration of a reactant is increased, then the system will respond to decrease it by favouring the forward reaction, which uses up the reactant. This shifts equilibrium to the right, increasing the concentration of the products and decreasing the concentration of the reactants. However, the concentration of the substance added will not return to its original concentration as the system can only partially counteract the change.

The partial pressure of a gas is the pressure exerted by that gas alone in a mixture of gases.

Alternatively, if the concentration of a product is decreased, then the system will favour the reaction that produces products to increase the concentration again. Therefore, the forward reaction will be favoured and equilibrium will shift to the right.

As the partial pressure of a gas is proportional to its concentration in a gaseous mixture, a change in the partial pressure can be considered as a change in concentration (Table C1.3).

Table C1.3 The effect of a change in concentration or partial pressure on equilibrium

Imposed change		Reaction favoured (forward or reverse)	Shift in equilibrium (left or right)	Resultant change in concentration or partial pressure of reactants	Resultant change in concentration or partial pressure of products
Product or reactant altered	Increase or decrease in concentration or partial pressure				
Reactant	Increase	Forward	Right	Decrease	Increase
Reactant	Decrease	Reverse	Left	Increase	Decrease
Product	Increase	Reverse	Left	Increase	Decrease
Product	Decrease	Forward	Right	Decrease	Increase

Consider the equilibrium established during the production of ammonia:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

If hydrogen gas is added to the container without a change in volume, then the concentration of hydrogen gas will increase. According to Le Chatelier's principle, the system will react to reduce this increased concentration, thus favouring the forward reaction, which uses up hydrogen gas. Therefore, the reaction will shift to the right, the concentrations of hydrogen gas and nitrogen gas will decrease, while the concentration of ammonia will increase.

Changes to volume

If the volume of a gaseous system is changed, then the concentration of all the gaseous substances will be altered. According to Le Chatelier's principle, the system will react to reverse the change in the total concentration (or pressure). To determine whether the forward or reverse reaction will achieve this change, you must consider the number of gaseous molecules in the reactant and products. The reaction that will produce more molecules of

gaseous substances will increase the total concentration or pressure, while the reaction that uses more molecules will decrease the total concentration or pressure.

For example, in the reaction between nitrogen gas and hydrogen gas to produce ammonia, 4 molecules are used to make 2 molecules.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$1 + 3 = 4$ 2

$\therefore$ 4 gas molecules used 2 gas molecules produced

If the volume of the system is decreased, then the total pressure will increase. According to Le Chatelier's principle, the system will react to decrease the total pressure. In this reaction, the forward reaction uses more molecules than it produces, thus decreasing the total number of particles and therefore pressure.

Changes to temperature

If the temperature of the system is increased, then according to Le Chatelier's principle the system will react so as to decrease the temperature. To do this, the endothermic reaction will be favoured as it uses up energy. Alternatively, if the temperature is decreased, then the exothermic reaction will be favoured in order to produce heat energy to increase the temperature.

Consider again the production of ammonia:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.4\,\text{kJ mol}^{-1}$$

This reaction as written is an exothermic reaction. Therefore, if the temperature of the system is increased, the endothermic reaction will be favoured to use up the added energy. This will favour the reverse reaction, resulting in an increase in the concentrations of hydrogen and nitrogen gas and a decrease in the concentration of ammonia. Conversely, if the temperature is decreased, then the exothermic reaction will be favoured. This will result in the forward reaction being favoured, increasing the concentration of ammonia and decreasing the concentrations of hydrogen and nitrogen gas.

Graphing changes to equilibrium

We can use graphs to show the concentrations or rate of reactions when there are changes to equilibrium.

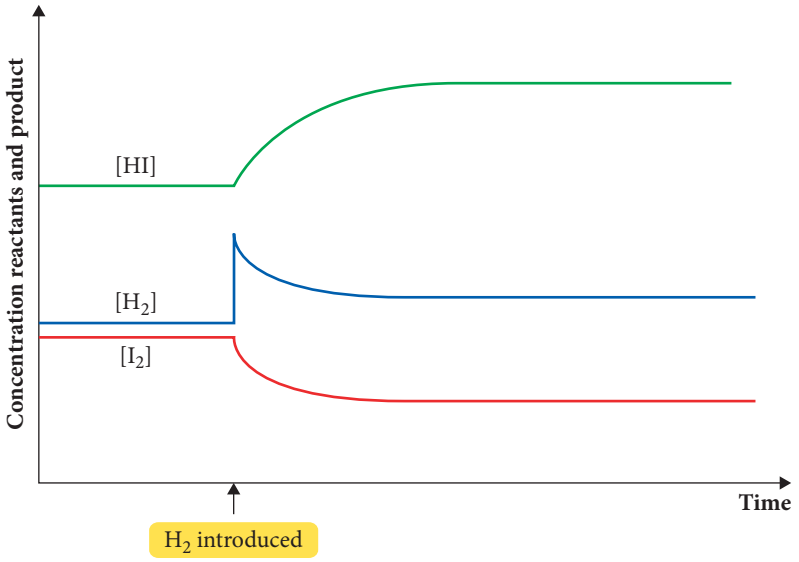
Graphing changes to concentration or partial pressure

When there is a change in concentration or partial pressure, there will be a sudden increase or decrease in the substance added or removed. The concentrations of all species will then change more gradually until the concentrations are constant when equilibrium is re-established.

Consider the reaction between hydrogen and iodine:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

If hydrogen gas is added to the system, then its concentration will suddenly increase (assuming the volume remains the same). In response, the forward reaction will be favoured. This will use up hydrogen and iodine, producing hydrogen iodide. Therefore, the concentration of hydrogen and iodine will decrease while the concentration of hydrogen iodide will increase. This can be represented on the graph in Figure C1.17.



◀ Figure C1.17
Concentrations of reactants and product when hydrogen gas is introduced for the reaction:
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

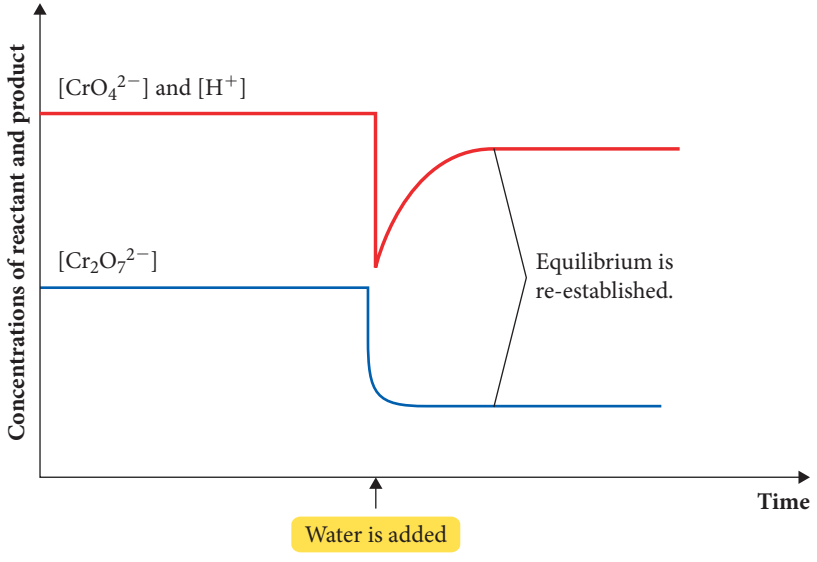
Graphing changes to volume or pressure

If the volume of a gas is altered, then the concentration of all the gases will change. This will be reflected on a graph by sudden increases or decreases in all these species. As the appropriate reaction is favoured, the concentrations will gradually change as equilibrium is being re-established. A similar trend is seen in aqueous species if water is added or removed from a solution.

Consider the equilibrium between chromate and dichromate:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

If water is added to the solution, then the concentration of all the aqueous substances will decrease. In aqueous solution the concentration of water is assumed to be constant. Therefore, on the graph there will be sudden drops in the concentration of chromate, hydrogen ions and dichromate. As four aqueous molecules are used to produce only one, the reverse reaction will be favoured. This will use up dichromate and produce chromate and hydrogen ions. Therefore, the concentration of chromate and hydrogen ions will increase while the concentration of dichromate will decrease until the concentrations once again plateau and remain constant.



◀ Figure C1.18
Concentrations of reactant and product following a change in volume

Graphing changes to temperature of a system at equilibrium

When the temperature of a system at equilibrium is altered, there are no sudden initial changes in concentration. This is reflected in a graph of concentration versus time by no sudden changes

in concentration. However, one reaction will be favoured as equilibrium is being re-established. Therefore, the concentrations will gradually change as the system counteracts the change.

To demonstrate this, we will consider the reaction between hydrogen gas and nitrogen gas to form ammonia. This reaction is exothermic:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.4 \text{ kJ}$$

If the temperature of the system is decreased, then the forward reaction will be favoured to counteract the change and produce more energy. This means that the concentration of ammonia will increase while the concentrations of hydrogen gas and nitrogen gas will decrease. This can be shown on the graph in Figure C1.19.

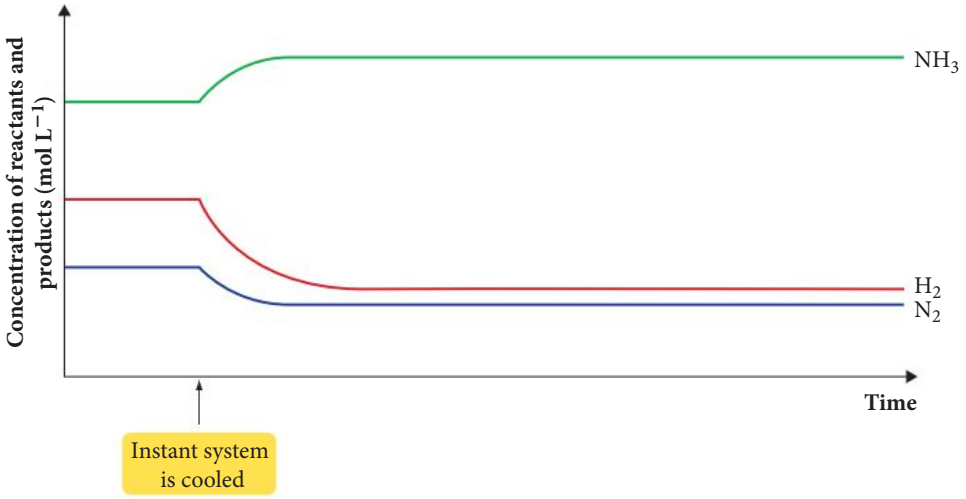


Figure C1.19 ▶ Concentrations of reactants and products during a decrease in temperature

Summary of identifiable changes on a graph

Table C1.4 summarises how changes to a system can be identified on a graph.

Table C1.4

Change to system	Key point on graph
Increase in concentration or partial pressure of one substance	Sudden increase in one substance
Decrease in concentration or partial pressure of one substance	Sudden decrease in one substance
Increase in volume/decrease in pressure	Sudden decrease in all gaseous species
Decrease in volume/increase in pressure	Sudden increase in all gaseous species
Increase in temperature	No sudden changes
Decrease in temperature	No sudden changes

QUESTION SET 1.3

Remembering

1 State the collision theory.

2 State Le Chatelier's principle.

Understanding

3 Describe the effect on the energy of particles if the temperature is decreased.

4 Explain why the volume of some gaseous systems can be altered without affecting the position of equilibrium.

Applying

5 Silver ions can be removed from solution by adding carbonate ions:

$$2Ag^+(aq) + CO_3^{2-}(aq) \rightleftharpoons Ag_2CO_3(s)$$

Describe two processes that would increase the amount of silver removed.

6 Soluble sodium hypochlorite pellets are used in swimming pools to help kill bacteria and algae:

$$ClO^-(aq) + H^+(aq) \rightleftharpoons HClO(aq) + \text{heat}$$

Use Le Chatelier's principle to predict the changes that would occur for each of the following (assume the pool is covered and is therefore a closed system).

a Adding more sodium hypochlorite pellets

b Adding sodium hydroxide

c The pool warming up during a hot day

CHAPTER CHECKLIST

You should know:

- the chemical system is all the chemicals involved in the reaction whereas the surroundings are everything around these chemicals
- chemical systems are closed if substances are unable to enter or leave or open if substances are able to enter or leave
- a reversible reaction occurs when the reactants can form products (the forward reaction) and the products are able to form reactants (the reverse reaction)
- a reaction will be reversible if the activation energy of both the forward and reverse reactions are able to be overcome
- dynamic equilibrium is a specific type of steady state where the amount of reactants and products remain constant as the rates of the forward and reverse reactions are equal. This is only achievable with a reversible reaction and a closed system
- as a system moves towards equilibrium the concentration of the reactants will decrease while the concentration of the products will increase until all concentrations remain constant. Simultaneously the rate of the forward reaction will initially be high, and decrease while the rate of the reverse reaction will initially be low, and increase. Equilibrium is reached when the rates of the forward and reverse reactions are equal and the concentrations of all species are constant.
- the equilibrium constant (K) reflects the relative proportion of the products and reactants. A high value of K indicates a high proportion of products and therefore a reaction that occurs to a significant extent. A low value of K indicates a low proportion of products and therefore a reaction that only occurs to a small extent.
- for the reaction $aA + bB \rightleftharpoons cC + dD$, K is calculated by using the equilibrium expression $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
- solids and liquids are not included in the equilibrium expression as their concentrations are unchanging
- the equilibrium constant is relevant for a specific reaction at a specific temperature
- changes to the conditions may lead to a change in equilibrium
- an increase in the concentration of a reactant will increase the rate of the forward reaction whereas an increase in the concentration of a product will increase the rate of the reverse reaction
- an increase in volume of a gaseous system will decrease the concentration of all gases. The reaction that produces the most number of gas molecules will have a greater increase in rate compared to the opposite reaction
- if the temperature is increased the endothermic reaction will increase its reaction rate more than the exothermic. Alternatively, if the temperature is decreased, then the endothermic reaction will decrease its reaction rate more than the exothermic reaction
- Le Chatelier's principle can be used to predict the effect when a change is made to a system at equilibrium
- in a graph of concentration versus time, a change in:
  - concentration will cause a sudden change in that concentration only
  - volume of a gaseous system will cause a sudden change in all gases
  - temperature will have no sudden changes.

CHAPTER GLOSSARY

activated complex an unstable state of high enthalpy where the bonds of the reactants have been broken but the new bonds of the products have yet to form

activation energy the energy needed to break the reactant's bond in order to form the products

chemical change a change that produces new substances

chemical system the chemicals involved in a reaction

closed system a chemical system in which no substances are able to enter or leave

collision theory the theory stating that for a reaction to proceed, the reactant particles must collide with sufficient energy and an appropriate orientation

dynamic equilibrium a state in which the amount of reactants and products remains constant as the rates of the forward and reverse reactions are equal

endothermic reaction a reaction that absorbs energy from the surroundings; the products have more energy than the reactants

enthalpy the total energy of a substance

equilibrium the state for a reversible reaction in a closed system when the forward and reverse reactions occur at the same rate

equilibrium constant (K) the value of the ratio between the concentration of the products and reactants

equilibrium expression the ratio of the concentration of products to reactants used to calculate the equilibrium constant

exothermic reaction a reaction that releases heat energy to the surroundings due to the products having less energy than the reactants

forward reaction the process of the reactants forming the products

Le Chatelier's principle a principle that predicts the effect of changes to a system at equilibrium: if a change is made to a system at equilibrium, the system will react to partially counteract the change

open system a chemical system in which substances are able to enter or leave

partial pressure the pressure exerted by a single gas in a gas mixture

physical change a change where no new substances are formed

reverse reaction the reaction in which the products form the reactants

reversible reaction a reaction in which the reactants become products and the products become reactants

steady state a state in which the properties remain constant

surroundings substances around the chemical system but not involved in the reaction

yield the amount or percentage of the possible product that is actually produced

CHAPTER REVIEW QUESTIONS

Remembering

1 State Le Chatelier's principle.

2 List the requirements for dynamic equilibrium.

Understanding

3 Describe what you would observe in a system at equilibrium.

4 Explain why solids and liquids are not included in the equilibrium expression for a heterogeneous system.

5 Describe the relative concentrations of reactants and products for a reaction with an equilibrium constant of 5.0×10^{-17}.

6 Use the concept of activation energy to explain why some reactions are not reversible.

Applying

7 Write the equilibrium expression for the ionisation of acetic acid in water.

8 Use collision theory to explain the effect of removing hydronium ions from the following reaction mixture at equilibrium.

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

9 For the reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = +57.2 \text{ kJ}$$

what would be the effect of each of the following changes on an equilibrium mixture of N_2O_4 and NO_2?

- **a** Adding N_2O_4
- **b** Adding $NO_2(g)$
- **c** Adding heat
- **d** Removing $N_2O_4(g)$
- **e** Increasing the pressure

10 Sketch a graph showing the relative concentrations of all species over time if equal amounts of NO and O_2 are introduced to a closed container and are allowed to reach equilibrium:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

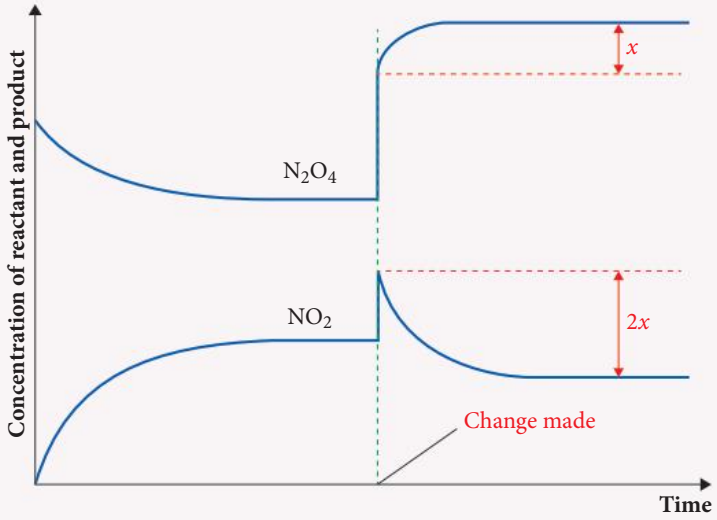
11 When copper(II) carbonate is heated, it decomposes into copper(II) oxide and carbon dioxide.
- a Write a balanced equation for the reaction.
- b Write the equilibrium expression for the reaction.
- c Describe what would happen at a molecular level if the container was open.
- d Describe what would happen at a molecular level if the container was closed.

Analysing

12 The graph in Figure C1.20 shows the concentration of the reactant and product for the reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Figure C1.20 ▶

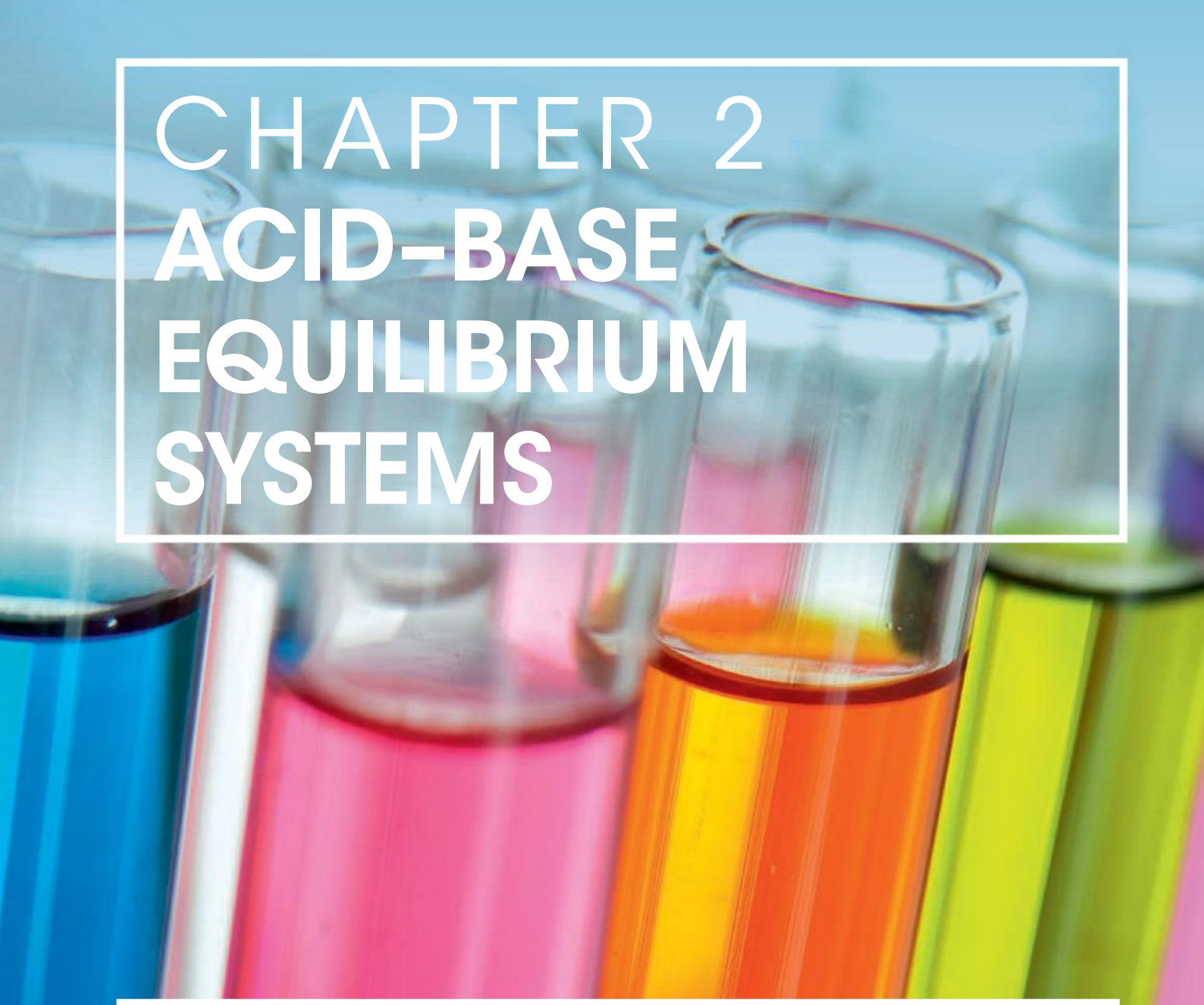


Use Le Chatelier's principle to explain the changes seen in the graph.

Reflecting

13 Research the role equilibrium plays in the transport of oxygen in our blood.

CHAPTER 2
ACID–BASE EQUILIBRIUM SYSTEMS



By the end of this chapter you will have covered the following material.

Science Understanding

- Equilibrium position can be predicted qualitatively using equilibrium constants (ACSCH096)
- Acids are substances that can act as proton (hydrogen ion) donors and can be classified as monoprotic or polyprotic depending on the number of protons donated by each molecule of the acid (ACSCH097)
- The strength of acids is explained by the degree of ionisation at equilibrium in aqueous solution, which can be represented with chemical equations and equilibrium constants (K_c) (ACSCH098)
- The relationship between acids and bases in equilibrium systems can be explained using the Brønsted–Lowry model and represented using chemical equations that illustrate the transfer of hydrogen ions (ACSCH099)
- The pH scale is a logarithmic scale and the pH of a solution can be calculated from the concentration of hydrogen ions; K_w can be used to calculate the concentration of hydrogen ions from the concentration of hydroxide ions in a solution (ACSCH100)
- Acid–base indicators are weak acids or bases where the acidic form is of a different colour to the basic form (ACSCH101)

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2.1 What is an acid?

In Chemistry Chapter 1, you learnt about dynamic equilbrium reactions and how the relative concentrations of products and reactants affect the position of equilibrium. You also learnt about how temperature and pressure affect the equilibrium system. Le Chatelier's principle can be applied to acid–base systems. Ancient Greeks identified sour-tasting substances as *oxein,* which was translated to Latin as *acetum* and later anglicised to the current name 'acid'. Later these substances were also found to change the colour of litmus paper and corrode metals (in the case of acids).

Bases were known to counteract the effects of acids. They were originally known as *alkaline,* from the Arabic word for roasting, due to the production of soap that involved roasting ashes and reacting them with water and slaked lime. During the 18th century, Antoine Lavoisier studied the composition and structure of these substances and began to inform our modern understanding of acids and bases. Early chemists could identify an acid or a base from its properties. But to develop a conceptual definition of an acid requires an understanding of the structure of the molecules or ions of acids and bases and the mechanism of acid–base reactions.



Figure C2.1 ▶ Acids and bases are everyday items. Examples of substances that contain acids are vinegar (ethanoic acid), lemon juice (citric acid) and aspirin (acetylsalicylic acid). Examples of substances that contain bases are oven cleaners (sodium hydroxide), some detergents and bicarbonate of soda.

You can use H^+ to represent the hydronium ion H_3O^+ provided that it is clearly understood that it is just an abbreviation.

In *Nelson Chemistry Units 1 & 2 for the Australian Curriculum*, an acid was defined as a substance that produces hydrogen ions (H^+), or more strictly hydronium ions (H_3O^+), in an aqueous solution. The reaction of the acid with water is called an **ionisation reaction**, as ions are formed. Acids in which almost all of the acid molecules ionise are defined as **strong acids**. Examples of strong acids are hydrochloric acid (HCl), nitric acid (HNO_3) and sulfuric acid (H_2SO_4). Acids in which only some of the molecules ionise are defined as **weak acids**. Examples of weak acids are vinegar (a solution containing acetic acid), citric acid, hydrofluoric acid (HF), lactic acid and carbonic acid (H_2CO_3).

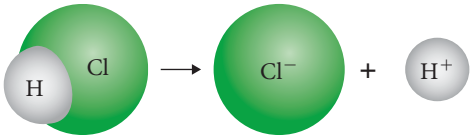


Figure C2.2 ▶ Strong acid ionisation: $HCl \rightarrow Cl^- + H^+$

EXPERIMENT 2.1

TESTING THE PROPERTIES OF ACIDS AND BASES

In Year 11 you were told that:

- acids have a sour taste, sting or burn the skin, conduct electricity in solution and turn blue litmus red
- bases have a bitter taste, slippery feel in aqueous solution, conduct electricity in solution (not all bases are soluble) and turn red litmus blue.

Aim

To test most of the properties for common acids and bases listed above, and for some common chemicals you will find at home

Materials

- 0.1 mol L^{-1} hydrochloric acid solution
- Citric acid
- 0.1 mol L^{-1} sodium hydroxide solution
- 0.1 mol L^{-1} sodium bicarbonate (sodium hydrogen carbonate) solution
- 50 mL beakers (one for each solution)
- Range of common chemicals such as detergent, coffee, lemon juice, milk
- Litmus paper (red and blue)
- Powerpack
- Leads
- Alligator clips
- Graphite rods
- Light bulb

Complete the risk assessment below to show any risks associated with completing this experiment and ways to manage them.

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Glassware may break and cut you.	Handle glass with care. Inspect and discard any chipped or cracked beakers, no matter how small the damage. Sweep up broken glass with a dustpan and brush; do not use fingers.
Litmus paper is flammable.	Store in dry location.
The powerpack may give an electrical shock.	Do not use if the cord is damaged or loose. Only use the powerpack if it is tagged as safe.
0.1 mol L^{-1} sodium hydroxide is slightly toxic.	Never ingest any laboratory chemicals.
Alligator clip	
Household chemical 1 (your choice)	
Household chemical 2 (your choice)	

Procedure

1. Predict whether your common chemical will be acidic, basic or neither.
2. Test each sample with a small strip of red litmus. Record the results.
3. Test each sample with a small strip of blue litmus. Record the results.
4. Test each sample for electrical conductivity by constructing an electrical circuit with the powerpack and light bulb.

Results

Record your results in an appropriately labelled table.

Analysis of results

1 If possible, classify whether each substance was acidic or basic.
2 What difficulties did you experience when testing the common chemicals?
3 Were your predictions correct?

Discussion

1 What trends did you observe?
2 Why must you not test for the properties of acids, such as sour taste, stinging or burning the skin? Or for the bitter taste or slippery feel of bases in aqueous solution?

Conclusion

1 How useful are the common properties for distinguishing acids from bases?
2 Do these descriptions allow you to distinguish other solutions as neither acid nor base?
3 What would be the advantage of having alternative ways of distinguishing acids and bases?

Taking it further

Acids and bases are added to many processed foods. For example, acids are added for taste to sour lollies. This is one way to safely taste acids. Add an acidic solution to a solution of sodium bicarbonate to see effervescence. Predict how self-raising flour works.

Design and carry out an experiment in which you make pancakes or a simple chocolate cake from plain flour and sodium bicarbonate rather than self-raising flour to safely test the taste of a base. This must be undertaken outside a class laboratory. Why is this a safer method than a simple taste test?

Table C2.1 Examples of acids and bases

Strong acids	Strong bases
Hydrochloric acid, HCl(aq) Nitric acid, HNO_3 Sulfuric acid, H_2SO_4	Sodium hydroxide, NaOH Potassium hydroxide, KOH Barium hydroxide, $Ba(OH)_2$ Sodium oxide, Na_2O
Weak acids	**Weak bases**
Ethanoic acid, CH_3COOH Carbonic acid, H_2CO_3(aq) Hydrofluoric acid, HF Citric acid, $C_6H_8O_7$	Ammonia, NH_3 Methylamine, CH_3NH_2

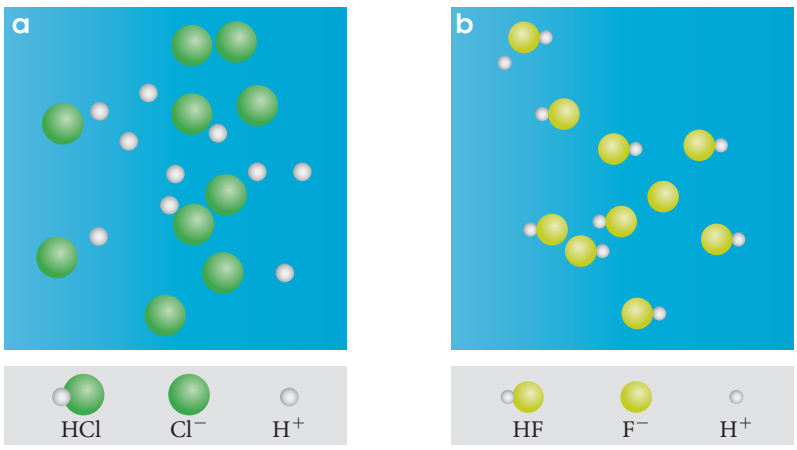
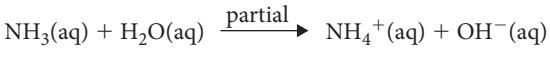


Figure C2.3 ▶ Comparison of how strong acid (HCl) and weak acid (HF) molecules ionise in water. a) All of the HCl molecules are ionised. b) Only some HF molecules are ionised.

A base can be considered as a substance that produces a hydroxide ion in solution; for example, soluble salts containing the oxide (O^{2-}) ion or hydroxide (OH^-) ion. A soluble base is called an alkali. **Strong bases** always dissociate in water to form separate ions. This reaction is called a **dissociation** reaction. Examples of strong bases are sodium hydroxide (NaOH) and potassium hydroxide (KOH). **Weak bases** such as ammonia (NH_3) have only a few ions dissociated in water.





ALUMINIUM CANS

Watch this video of the reaction of aluminium cans with an acid and a base.

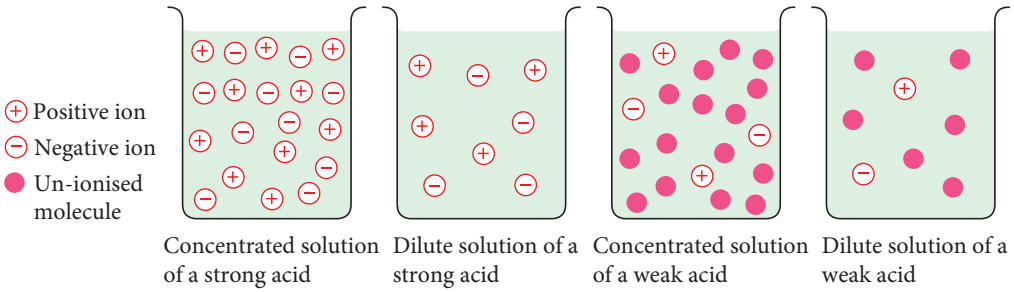
Concentration versus strength

The strength of an acid or base refers to its ability to ionise in solution. Stronger acids ionise completely in solution. If the concentrations of a strong acid and a weak acid are the same, the concentration of hydronium ions [H_3O^+] is higher in the strong acid solution than in the weak acid solution. Only a few particles of weak acid dissociate, so there is a lower concentration of weak acid ions in aqueous solution so a solution of a weak acid has a lower concentration of hydronium ions.

You will recall from Year 11 that the definitions of concentrated and dilute relate to the amount of solute in a specified amount of solution. The most convenient measure of concentration used in chemistry is molarity.

- A concentrated solution is one in which the total concentration is high; for example, 4 M or 4 mol L^{-1}.
- A dilute solution is one in which the total concentration is low; for example, less than 2 M or 2 mol L^{-1}.

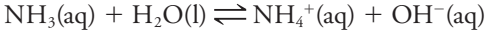
It is possible to have a dilute solution of a strong acid and a concentrated solution of a weak acid. This is also true of strong and weak bases. 'Concentrated', 'dilute', 'strong' and 'weak' have independent meanings in chemistry as shown in Figure C2.4.



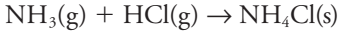
◀ **Figure C2.4** Concentrated and dilute solutions of a weak and strong acid

The ammonia dilemma

The weak base ammonia challenged the early chemists' definition of a base. The dilemma facing chemists was that either ammonia was not a base or their definition was inaccurate or incomplete. Some chemists argued that the definition was acceptable because when ammonia reacts with water, the following reaction occurs:



But ammonia gas reacts with hydrochloric acid fumes to form ammonium chloride. There is no water and no OH^- or O^{2-} ions are involved, as shown in the reaction:



This reaction showed that the original definition of an acid and a base needed to be redefined.

Anhydrides are oxides that do not contain an H^+ or OH^- ion unless they react with water.

EXPERIMENT 2.2

WHITE SMOKE (TEACHER DEMONSTRATION ONLY)

Bases, such as ammonia, were originally described by their reaction with water. They produced hydroxide ions (OH^-) and by definition the hydroxide ions gave the basic nature to the substance. When water is not present, will ammonia still act as a base? In this reaction, fumes from hydrochloric acid react with the gaseous ammonia, forming a white smoky substance when they meet.

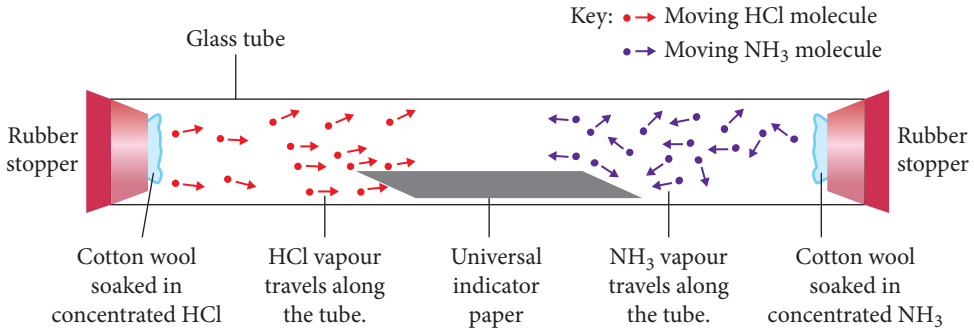
Aim

To demonstrate that acid and base reactions can occur without water

Materials

- Concentrated ammonia solution (15M)
- Concentrated hydrochloric acid (10M)
- Glass tubing at least 500cm long and 2cm wide
- Retort stands with bosses and clamps
- Cotton wool
- Bungs with small hole to hold cotton wool
- Universal indicator paper may also be used

Figure C2.5 ▶ The reaction between ammonia gas and hydrogen chloride gas



What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Ammonia gas and concentrated ammonia solution (15–16M or 28–30% w/w) is highly irritating to the lungs due to the ammonia gas evolved. It is corrosive to skin and eyes and may cause asthma attacks.	This is a teacher demonstration only. Avoid inhalation of extremely pungent vapour. Do not mix it with halogens or materials that release halogens. Wear gloves and safety glasses and perform the demonstration in a fume hood.
Concentrated hydrochloric acid (variable 10–12M, 32–37% w/w; density 1.16–1.18 g mL^{-1}) is highly toxic and irritating to the lungs due to the HCl gas evolved. It is highly corrosive to skin and eyes and toxic if ingested.	Wear gloves and safety glasses and perform the demonstration in a fume hood. Do not breathe vapour. Avoid splashes in eyes or on skin.
Glassware may be cracked or broken.	Handle glass with care. Inspect and discard any chipped or cracked beakers, no matter how small the damage. Sweep up broken glass with a dustpan and brush; do not use fingers.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Use the clamps and retort stand to ensure that the glass is secure and horizontal in a functioning fume hood. Ensure that the bottles are also in the fume cupboard. If universal indicator paper is being used, place it in the glass tube.
2. Open the bottle of ammonia solution cautiously. Ensure that the mouth of the bottle is not facing anyone.
3. Dip one of the cotton wool wads into the ammonia solution and then quickly secure it in the glass tube and replace the lid back on the ammonia bottle.
4. Repeat steps 2 and 3 with the other cotton wad and the hydrochloric acid solution.

Results

Observe what occurs in the glass tube.

Analysis of results

1 What was the most likely substance that formed?

2 If a strip of universal indicator paper was used, what colour did it turn?

Discussion

1 Write the equation for the reaction that occurred between ammonia and hydrochloric acid.

2 Which reactant acted as a base? Which one acted as an acid?

Conclusion

Is ammonia acting as a base in this case? Is the definition of a base as a substance that produces OH^- or O^{2-} ions justified by this experiment?

Taking it further

1 Why is it important that only the vapours are used?

2 Explore how the vapours travel in the tube. Explain the white smoke.

Redefining acids: Brønsted–Lowry acids

Chemists such as Lavoisier, Davy, Justus von Liebig and Arrhenius each took their turn in defining acids and bases. It was the Danish chemist Brønsted and the English chemist Lowry who refined the definition of acids and bases by taking ammonia into account.

An acid is a substance that donates one or more protons or hydrogen ions (H^+).
A base is redefined as a substance that accepts one or more protons.

The Brønsted–Lowry definition of acids and bases is broader than the original definition. In the reaction between ammonia gas and fumes of hydrochloric acid:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

Ammonia accepts a proton to form an ammonium ion (NH_4^+) and is acting as a base. HCl is acting as an acid as it donates a proton to form a chloride ion (Cl^-).

When hydrochloric acid molecules react with water, the HCl molecules are acting as an acid and the water molecules are acting as a base. The hydrochloric acid ionises to form hydronium ions (H_3O^+) and chloride ions (Cl^-). The water molecules are acting as a base because they accept H^+ ions.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

In the reaction of ammonia with water:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$



$NH_3(aq) + H_2O(l) \longrightarrow OH^-(aq) + NH_4^+(aq)$

◀ **Figure C2.6**
Reaction of the ammonia molecule with water to form a hydroxide ion and an ammonium ion

Sodium hydroxide is still categorised as a strong base in this definition. According to the Brønsted–Lowry definition of acids and bases it is more correct to say that NaOH is an ionic compound that is the source of the strong base OH^-.

In this example, ammonia is acting as a base and water is acting as an acid. In these two examples, water is capable of acting as an acid and a base. The water is **amphiprotic** – it can accept or donate a proton and so can act as an acid or as a base.

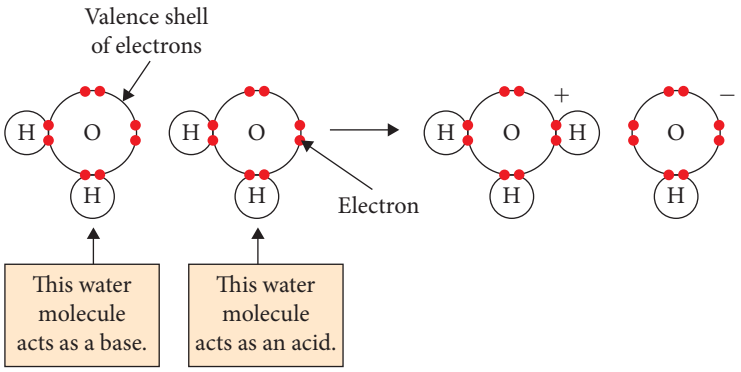


Figure C2.7 ▶ The amphiprotic nature of water. Water can act as an acid and as a base. It depends on what species is present.

In Nelson Chemistry Units 1 & 2 for the Australian Curriculum, *the term amphoteric was used to describe a substance that can act as an acid or a base. Effectively, the terms amphiprotic and amphoteric are interchangeable as a substance acts as an acid by donating a proton.*

The Brønsted–Lowry definitions of an acid as a proton donor and a base as a proton acceptor meant that bases became the mirror companion of acids, merely simple receptors. The measurement of hydronium ion concentration became key to defining the degree of acidity.

WOW

Superacids

Faster at corroding than sulfuric acid, 2×10^{19} times more powerful, unlike other acids able to react with hydrocarbons, breaking down raw petroleum and worthy of a Noble Prize (1994). Look, it is a superacid!

The alchemists thought that vinegar (acetic acid) was a strong acid. Sulfuric acid (oil of vitriol) was the strongest acid known for centuries. With a better definition of acids, chemists were able to develop superacids that are a million times stronger than earlier acids. In 1927, the first superacids were made by reacting sulfuric acid with fluorosulfuric acid and fluoroantimonic acid. Superacids are widely used in industry, and have applications in fuel cells and batteries. They also have the potential to clean up pollution in exhausts.

ACID STRENGTH

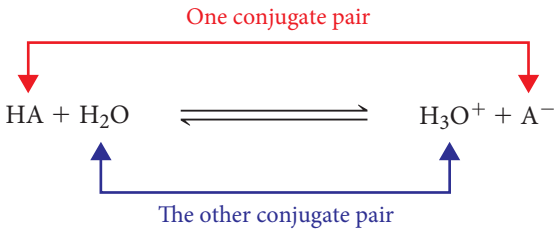
Watch this video to learn more about weak, strong and superacids.

Mirror companions and conjugate pairs

The Brønsted–Lowry definition of a base as the mere receptor of a proton allows the reactions of acids to be generalised. The reactions can be considered reversible as shown in the following equation where HA denotes an acid molecule:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

For the forward reaction, HA is an acid because it is donating a proton to the water. The water is a base as it accepts a proton from HA. The reverse reaction is a reaction between the hydronium ion and the A^- ion. H_3O^+ is an acid because it is donating a proton to the A^- ion. The A^- ion is a base that accepts a proton from the H_3O^+. This reversible reaction contains *two* acids and *two* bases. The pairs are called **conjugate pairs**.



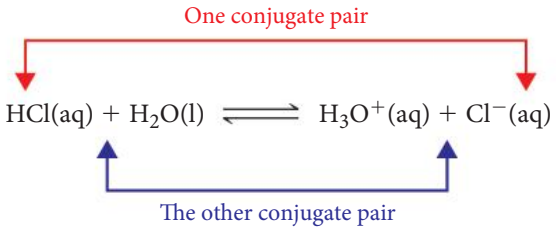
SUPERACIDS

Watch this video about how superacids are being used to clean up pollution.

When the acid, HA, loses a proton, it forms a base, A^-. The base, A^-, accepts a proton back again to re-form the acid, HA. HA and A^- are a conjugate pair, like an object and its image in the mirror except here the HA and the A^- are on either side of the arrows and are not identical.

Members of a conjugate acid–base pair differ from each other by the presence or absence of the transferable H^+ (hydrogen ion).

For example, HCl donates a proton to form its **conjugate base**, Cl^-. Water is acting as the base and forms its **conjugate acid**, H_3O^+.



QUESTION SET 2.1

Remembering

1 What was the earliest definition of acids and bases?

2 Identify the strong acids or strong bases in the following list.

Ammonia solution, $NH_3(aq)$

Carbonic acid, $H_2CO_3(aq)$

Nitric acid, $HNO_3(aq)$

Hydrochloric acid, HCl(aq)

Sodium hydroxide, NaOH(aq)

3 Identify the two conjugate acid–base pairs in each of the following equations:

a $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

b $NH_4^+(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NH_3(aq)$

c $HSO_4^-(aq) + O^{2-}(aq) \rightarrow SO_4^{2-}(aq) + OH^-(aq)$

d $H_2PO_4^-(aq) + CO_3^{2-}(aq) \rightarrow HPO_4^{2-}(aq) + HCO_3^-(aq)$

e $HC_2H_3O_2(aq) + HS^-(aq) \rightarrow C_2H_3O_2^-(aq) + H_2S(aq)$

4 Write the conjugate acids of the following bases.

a HCO_3^-

b OH^-

c HPO_4^{2-}

Understanding

5 Can an acid be both a strong acid and a dilute acid? What is meant by these terms?

6 Carbonates are bases. The earlier definitions could not account for the behaviour of carbonates but the Brønsted–Lowry definition can. Explain why.

Applying

7 The equation of the reaction between a solution of ammonium chloride and a solution of sodium hydroxide is:

$NH_4Cl(aq) + NaOH(aq) \rightarrow NH_3(aq) + H_2O(l) + NaCl(aq)$

Which substance is acting as an acid and which is acting as a base? Explain your reasoning.

8 Why would aqueous solutions of strong acids and bases be better electrical conductors than aqueous solutions of weak acids and bases? Would sulfuric acid $H_2SO_4(aq)$ be a better conductor than HCl? Explain.

Analysing

9 What is the difference between an ionisation reaction of HCl and a dissociation reaction of sodium hydroxide? Write the ionic equations of hydrochloric acid with water and sodium hydroxide with water to explain this difference.

2.2 The importance of the pH scale

The pH scale reflects the importance of the Brønsted–Lowry definition of an acid as a proton donor. The pH scale is a measure of the concentration of hydronium ions. The concentration can vary widely, generally from 10 M to 10^{-15} M. This range is extremely large so chemists have introduced a convenient scale called the pH scale to measure the concentration of the hydronium ion. The pH scale can indicate the acidic or basic nature of substances.

The square brackets around a species mean 'molar concentration of', so $[H_3O^+]$ is read as the molar concentration of hydronium ions.

The pH of a solution is defined as the negative logarithm (to the base 10) of the hydronium ion concentration:

$$pH = -\log_{10}[H_3O^+]$$

The pH scale was explored in Year 11. Recall that a change of 1 unit of pH is the same as changing the concentration of the solution by a factor of 10. This is due to the logarithmic pH – a change in concentration of H_3O^+ ion in solution by a factor of 10.

For a solution in which $[H_3O^+] = 0.1$ M (or 10^{-1}), the pH is 1.0

For a solution in which $[H_3O^+] = 0.01$ M (or 10^{-2}), the pH is 2.0

For a solution in which $[H_3O^+] = 0.000\,0001$ M (or 10^{-7}), the pH is 7.0.

Notice that $[H_3O^+] = 10^{-pH}$.

When determining the significant figures in pH values, only the mantissa (the digits after the decimal place) is significant; for example, a pH of 3.14 has only two significant figures. The '3' is called the characteristic and is a 'place holder'.

It is relatively straightforward to work out the pH when the concentration is 0.1 or 0.01, or any factor of 10. When the concentration is 0.015, which is between 0.1 and 0.01, you need a calculator. The following formula is used:

$$pH = -\log [H_3O^+]$$

For $[H_3O^+] = 0.015$ M, the pH is 1.82.

$$[H_3O^+] = 10^{-pH} \text{ or } pH = -\log_{10}[H^+]$$

A change in pH of one unit corresponds to a tenfold change in $[H_3O^+]$.

WORKED EXAMPLE 2.1

a Calculate pH, given $[H^+] = 1.0 \times 10^{-5}$ M.

b Calculate $[H^+]$ when pH = 8.5.

Answer

a pH = 5.0

b $[H^+] = 3.2 \times 10^{-9}$ M

Logic

a Choose correct formula and insert numbers.

$pH = -\log_{10}[H^+]$

$pH = -\log_{10}(1.0 \times 10^{-5})$

b Choose correct formula and insert numbers.

$[H^+] = 10^{-pH}$

$[H^+] = 10^{-8.5}$

Try these yourself

a Determine the pH of a solution, given $[H^+] = 0.001$ M.

b Determine the pH of a solution, given $[H^+] = 1.2 \times 10^{-5}$ M.

c Calculate $[H^+]$ when the pH of the solution is 6 and when it 11.7.

Polyprotic acids

Acids such as HCl and HNO_3 will give up one proton (hydrogen ion) per molecule. These are called **monoprotic**. A 0.1 M solution of a strong monoprotic acid will have a pH of 1, because all the acid molecules ionise. A 0.1 M solution of a weak acid will have a pH of >1 because only some weak acid molecules ionise, so the $[H^+]$ will be <0.1 M. Weak acids do not ionise completely.

Other acids can donate more than one proton. These acids can be strong, such as sulfuric acid, or weak, such as malic and citric acids. These acids are called **polyprotic** acids. The term 'polyprotic' refers to the ability to donate protons, *not* how readily these protons ionise in water. **Diprotic** acids can donate two protons.

Polyprotic acids can donate more than one proton per molecule. Diprotic acids donate two protons and may have a higher concentration of hydronium ions than the same concentration of a monoprotic acid.

SIGNIFICANT FIGURES

Visit this website to learn more about how to determine significant figures, including for pH.

pH of polyprotic acids

The pH of a 0.1 M solution of sulfuric acid (H_2SO_4) is around 0.69, not 1.0, which means it is a more acidic solution. The pH indicates that there are more hydronium ions than 0.1 M. The pH value can be used to calculate the concentration of hydronium ions $[H_3O^+]$ as almost 0.2 M. This is because sulfuric acid reacts with water as shown:

$$H_2SO_4(l) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H_3O^+(aq)$$

The complete ionisation of sulfuric acid occurs in two steps:

$$H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + H_3O^+(aq)$$

The second step involves the conjugate base of sulfuric acid, HSO_4^-. This is a weaker acid than sulfuric acid and not all of the molecules will react with water and ionise. So the concentration of hydronium ions is not quite twice the concentration of the acid. However, in neutralisation reactions, both protons will be donated. Effectively, the diprotic acid requires twice the number of moles of base. Le Chatelier's principle can be applied here.

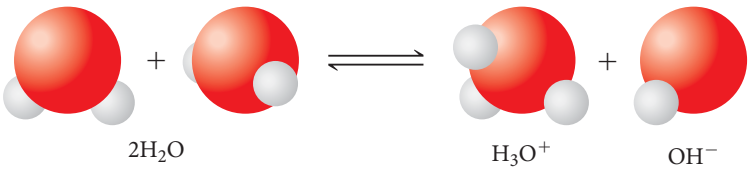
For each molecule of acid, the number of protons that may be donated is two. The concentration of the acid may be 0.1 M but as two protons can be donated when reacting with strong bases, this must be taken into account. Strong diprotic acids have a hydronium ion concentration greater than a monoprotic acid.

Other acids such as phosphoric acid (H_3PO_4) can donate three protons and are called **triprotic** acids and again the second and third steps involve weak acids.

2.3 Self-ionisation of water

The pH scale can also be used to measure indirectly the strength of alkaline solutions. This is because bases accept a proton from an acid. A substance cannot act as an acid without another substance acting as a base. The key to unlocking this came from understanding the reactions of water.

Water's amphiprotic nature means that it will react with itself to form hydronium and hydroxide ions as shown in Figure C2.8. This is an equilibrium reaction.



◀ Figure C2.8
Water reacts with itself in an equilibrium reaction to form hydronium and hydroxide ions, which shows water's amphiprotic nature.

Water conducts electricity to a small extent as it undergoes self-ionisation, according to the equation:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

This reaction occurs only to a very small extent. This is a reversible reaction and the equilibrium constant is small. The concentration of water is very large (approximately 55 M) and so effectively does not change significantly in the reaction, so $[H_2O]$ can be removed from the equilibrium expression. To represent this, the **self-ionisation constant, K_w**, the ionic product constant for water, is used:

$K_w = [OH^-][H_3O^+]$, where $K_w = 10^{-14}\,M^2$ at 298 K.

In pure water, the concentration of OH^- equals the concentration of H_3O^+:

$$[OH^-] = [H_3O^+]$$

This means $K_w = [OH^-][H_3O^+] = 10^{-14}\,M^2$ at 298 K.

$$= [H_3O^+]^2$$

$$[H_3O^+] = \sqrt{10^{-14}}$$

$$= 10^{-7}\,M$$

At 298 K, when water is neutral, $[H_3O^+] = [OH^-] = 10^{-7}$ M. The pH at this temperature is 7. This is true *only* when the temperature is 298 K (25°C).

When $[H_3O^+] > [OH^-]$, the solution is considered acidic. At 298 K, this is when $[H_3O^+] > 10^{-7}$ M.

When $[H_3O^+] < [OH^-]$, the solution is considered basic or alkaline. At 298 K this is when $[H_3O^+] < 10^{-7}$ M.

ACTIVITY 2.1

H_3O^+ IONS IN WATER

Aim

To estimate the number of $H_3O^+(aq)$ ions in a single drop of:

- water
- 1.0 mol L^{-1} HCl
- 1.0 mol L^{-1} NaOH

You will need

- Calculator
- Internet access
- 10 mL measuring cylinder
- Pipette
- Water

What to do

This problem may seem impossible to solve but by discussing the problem and recalling previous lessons, you should be able to get answers. You can use textbooks, data books and other resources. Ask for assistance if necessary.

1. In groups of two or three, discuss the problem and carry out any necessary practical work to try to work out answers. Make sure you get your method checked before starting on any practical work.
2. Discussion can play a vital role as it can stimulate ideas. Spend about 10 minutes on the initial discussion.

What did you discover?

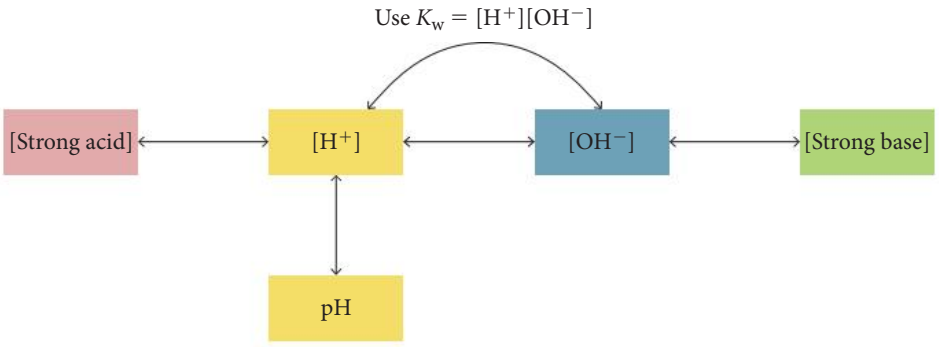
1. Write a brief account of what you did.
2. Prepare a short presentation aimed at 14–16-year-old students to be delivered to your class. Every group member should take part. Outline the problem and try to put the figures that you obtained into some context then present your solution.
3. Be prepared to answer questions and discuss what you discovered.

Calculating the pH of alkaline solutions

If an alkaline solution has a known concentration of hydroxide ion, $[OH^-]$, you can calculate the pH from the relationship:

$$K_w = [OH^-][H_3O^+] = 10^{-14}$$

Once the hydronium ion concentration, $[H_3O^+]$, is known, the pH can be calculated. Figure C2.9 shows a pathway that can be used to perform the pH calculations for strong acids and bases. The skill is in recognising what is given and what has to be determined.



◀ **Figure C2.9**
Pathway for performing pH calculations for strong acids and strong bases

In a 0.01 M solution of NaOH, $[OH^-] = 0.01$.

$$\text{So } [H_3O^+] = \frac{10^{-14}}{[OH^-]}$$

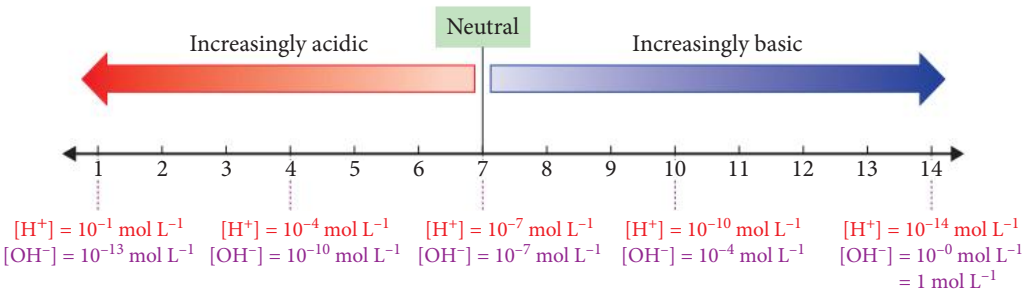
$$= \frac{10^{-14}}{10^{-2}} = 10^{-12}$$

$$\text{So pH} = -\log[H_3O^+] = -\log 10^{-12} = 12$$

Table C2.2 lists the pH values for solutions and corresponding $[H_3O^+]$ and $[OH^-]$. Notice that the pH scale 0–14 corresponds to these values. This range is due to the K_w of water, which is equal to 10^{-14} at 25°C.

Table C2.2 pH values for solutions and the corresponding hydronium and hydroxide ion concentrations

pH	1.0	3.0	5.0	7.0	9.0	11.0	13.0
$[H_3O^+]$	10^{-1}	10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}	10^{-13}
$[OH^-]$	10^{-13}	10^{-11}	10^{-8}	10^{-7}	10^{-5}	10^{-3}	10^{-1}



◀ **Figure C2.10**
The pH scale

WORKED EXAMPLE 2.2

Find the pH of a 0.02 M solution of sodium hydroxide.

Answer

pH = 12.3

Logic

1 Determine the species present.

NaOH is a strong base and dissociates 100% in solution.

2 Determine $[OH^-]$.

$NaOH \rightarrow Na^+ + OH^-$

Therefore, $[OH^-]$ = original [NaOH] = 0.02 M.

3 Choose the correct formula and insert the correct numbers.

$K_w = [H^+][OH^-] = 1 \times 10^{-14}$

$= [H^+][0.02] = 1 \times 10^{-14}$

Hence, $[H^+] = \dfrac{1 \times 10^{-14}}{0.02} = 5 \times 10^{-13}$

$pH = -\log[H^+] = 12.3$

Try these yourself

a Barium hydroxide is a strong base. Determine the pH of a 0.02 M barium hydroxide solution.

b If the pH of the NaOH solution was 9.5, what was the concentration of the solution?

Changing the pH of pure water

The pH scale was determined by using the K_w of water at 25°C (or 298 K). Pure water does not always have a pH of 7 because, as with all equilibrium reactions, the K_w value changes with temperature.

The self-ionisation of water is an equilibrium reaction as shown by:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

This is an endothermic reaction and the forward reaction will be favoured when the temperature is increased.

ACTIVITY 2.2

THE CHANGING pH OF PURE WATER

Aim

To determine the pH of pure water at different temperatures

What to do

1 The K_w values for water at various temperatures are given in the following table. Using a calculator, calculate the pH of the pure water for each of the given temperatures.

Temperature (°C)	K_w	pH
0	0.114×10^{-14}	
20	0.681×10^{-14}	
40	2.92×10^{-14}	
50	5.5×10^{-14}	
100	55×10^{-14}	

2 Graph pH against temperature, including pH of 7 for 25°C.

What did you discover?

1 Can you see a trend in your results? Explain.
2 Why is pH an indicator for the extent of the self-ionisation of water?
3 As temperature increases, what happens to pH?
4 Is water at 5°C and at 100°C acidic, basic or neutral? Explain.
5 Use the graph to determine the K_w of water at 80°C.

Redefining neutral solutions

You will recall from Year 11 that the definition of neutralisation is the reaction of an acid and a base to form salt and water. According to this definition, if the correct amounts of acid and base are mixed, then the resultant solution is neutral, neither acidic nor basic. If the solution is not neutral, it is because one reactant was in excess. A pH of 7 is considered neutral. However, this is only true when strong acids are reacted with strong bases.

An acidic solution has a concentration of hydronium ions above 10^{-7} and a basic solution has a concentration of hydronium ions below 10^{-7}. This is true only for 25°C. The more robust definition for a neutral solution becomes:

A solution is neutral when $[H_3O^+] = [OH^-]$. Pure water is neutral at all temperatures but the pH varies with temperature.

If an acid reacts with a different base (not the conjugate base and not water), it will always react completely. This means that the same calculations are used to determine the amount needed for neutralisation for both weak and strong acids. Determining the pH of the final solution for strong acids or strong bases is straightforward, as shown in Worked example 2.3. The pH determination for weak acids and bases is not so straightforward.

WORKED EXAMPLE 2.3

If 25 mL of a 0.50 mol L^{-1} solution of NaOH was added to 75 mL of a 0.3 mol L^{-1} solution of H_2SO_4, then what would the pH of the final solution be?

Answer

pH = 0.488

Logic

1 Write a balanced equation.
$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$
or $H_3O^+ + OH^- \rightarrow 2H_2O$ (but remember that H_2SO_4 is diprotic)

2 Calculate the number of moles of H_2SO_4 and NaOH using $c = \frac{n}{V}$.
$c(NaOH) = 0.50$ mol L^{-1} $V = 25$ mL $= 0.025$ L $n = ?$
$0.50 = \frac{n}{0.025}$
$n(NaOH) = 0.50 \times 0.025 = 0.0125$ mol
$c(H_2SO_4) = 0.30$ mol L^{-1} $V = 75$ mL $= 0.075$ L $n = ?$
$0.30 = \frac{n}{0.075}$
$n(H_2SO_4) = 0.30 \times 0.075 = 0.0225$ mol

3 If the solution was neutral, then $[H_3O^+] = [OH^-]$. Determine which reactant is in excess.
$n(NaOH) = 0.0125$ mol
$n(H_2SO_4) = 0.0225$ mol, $n(H_3O^+) = 0.0450$ mol
H_2SO_4 is in excess by $0.045 - 0.0125 = 0.0325$ mol

4 Calculate $[H_3O^+]$.

Using $c = \frac{n}{V}$, $V = 25\,mL + 75\,mL = 0.100\,L$

$[H_3O^+] = \frac{0.0325}{0.100} = 0.325\,M$, $[H_3O^+]$ is in excess.

5 Calculate the pH.

$pH = -\log [H_3O^+] = 0.488$

Try these yourself

a What is the resultant pH when 50 mL of 0.1 M NaOH is added to 100 mL of 0.1 M HCl.

b How many grams of barium hydroxide is required to neutralise 500 mL of 0.2 M nitric acid?

c How much 0.1 M NaOH is required to neutralise 100 mL of 0.277 M ethanoic acid solution.

Salts: not necessarily neutral

The equivalence point in titrations for weak acids and weak bases is not at pH 7 because of the acidic or basic nature of the conjugate pairs.

Another factor that influences the pH of the final solution is the salt produced after the reaction of an acid with a base. Salts are ionic compounds produced when an acid neutralises a base. They are formed during the neutralisation reaction when a proton is transferred from the acid to the base. This reaction forms a new conjugate base and a new conjugate acid. A solution of the salt may be acidic, basic or neutral. Earlier definitions of acids and bases could not explain why. The Brønsted–Lowry theory of acids can explain it: the conjugate acids or bases (the ions) formed may react with water.

Strong acids have very weak conjugate bases. Strong bases have very weak conjugate acids. These cannot react with water and are neutral. For weak acids, the conjugate bases are stronger. They will then react with water to form a basic solution. For weak bases, the conjugate acid will react with water to form an acidic solution.

EXPERIMENT 2.3

AMPHIPROTIC NATURE OF SALTS

When amphiprotic materials react with water, they can either donate or accept protons. Measuring the pH will determine if the solution is relatively acidic or basic.

If $[H^+] > [OH^-]$, then $pH < 7$, and the substance is acting as an acid. If $[H^+] < [OH^-]$, then $pH > 7$, and the substance is acting as a base.

The sodium salt for each sample is used. The Na^+ ion is a spectator ion and will not play a role in the reactions.

Aim

To test salts for their acid and base strength

Materials

- 0.1 M $NaHCO_3$
- 0.1 M $NaHSO_4$
- 0.1 M Na_2HPO_4
- 0.1 M NaH_2PO_4
- Universal indicator and chart
- Micro test tubes and rack

Complete the risk assessment box to show any risks associated with completing this experiment and ways to manage them.

What are the risks in doing this experiment?	How can you manage these risks to stay safe?

Procedure

1 Place 20 drops of each salt solution into a separate micro test tube.
2 Add 1–2 drops of universal indictor to each sample.
3 Use the chart to determine the pH of the solution.

Results

1 Record the resultant pH for each solution.
2 Determine $[OH^-]$ and $[H_3O^+]$ for each sample, assuming the temperature is 25°C.
3 Determine the pH of 0.1 M samples of HCl and NaOH. Compare the values obtained to the calculated value of a strong acid and strong base.

Analysis of results

1 List the samples from the lowest pH to the highest pH.
2 Which sample is the most acidic?
3 Which sample is the most basic?

Discussion

1 Write the reaction with water for each sample.
2 Decide for each sample if the salt was an acid or a base. Explain your reasoning.
3 Why could a pH meter not be used?

Conclusion

1 Compare the pH results obtained for each sample.
2 Are the salts acidic or basic?
3 Discuss whether the results allow the determination of the acid and base strength of the amphiprotic salts.

QUESTION SET 2.2

Remembering

1 Define:
   a diprotic.
   b amphiprotic.
2 When placed in a beaker of water, which of the following will ionise completely?
   HCl, NaOH, glucose ($C_6H_{12}O_6$), HNO_3, NaCl, $CuSO_4$, water, ethanoic acid
3 What is the K_w of water at 25°C?

Understanding

4 Determine the concentrations of H_3O^+ and OH^- in aqueous solutions of:
   a black coffee, pH = 5.0.
   b oven cleaner, pH = 14.0.
   c cola drink, pH = 3.
   d toothpaste, pH = 8.
5 Arsenic acid has the formula $H_3AsO_4(aq)$. Would you expect it to be a monoprotic, diprotic or triprotic acid? Explain.

Applying

6 a Determine the pH of each of the following strong electrolytes.
   i 0.01M HNO_3
   ii 0.005M $Ca(OH)_2$
   iii 1M HCl
   iv 0.1M NaOH
   v 0.005M H_2SO_4
   vi 0.230M hydrochloric acid
   vii 0.0175M nitric acid
   viii 1.27M hydrochloric acid
   b Determine the pH when $[H_3O^+] = 3.33 \times 10^{-5} mol L^{-1}$.

7 What is the molarity of the following solutions?
   a 20 mL of HCl with a pH of 3
   b NaOH solution with a pH of 11.5
   c 300 mL of a calcium hydroxide solution with a pH of 10
   d Sulfuric acid with a pH of 3

Analysing

8 What is the resultant pH when:
   a 50 mL of 0.2 M HCl is added to 100 mL of 0.1 M NaOH?
   b 100 mL of a solution of pH 6 is diluted with 100 mL of water?

2.4 Acidity constants

The symbol '(aq)' refers to the species hydrated by water molecules. As such, HCl(aq) effectively does not exist. Rather, $H^+(aq)$ and $Cl^-(aq)$ exist. For strong acids, bases and salts, the ionised form is the best representation.

In a weak acid, only some of the acid molecules ionise. This means that there is equilibrium between the acid and the conjugate base; for example, the weak acid HF:

$$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$$

The equilibrium expression for this reaction is:

$$K = \frac{[H_3O^+][F^-]}{[HF][H_2O]}$$

Rearranging the formula gives:

$$K[H_2O] = \frac{[H_3O^+][F^-]}{[HF]}$$

Water is the solvent and the concentration of water does not alter significantly; it is effectively constant at 55.5 mol L^{-1}. This means that it can be incorporated into K. This now forms the **acid dissociation equilibrium constant**, K_a. K_a represents a weak acid in an aqueous solution.



To see what acids are in wine, refer to Context 1, 'Wine', page 10.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

When the weak acid hydrofluoric acid dissolves in water, only a small percentage of the molecules ionise. The extent of the forward reaction is very small. The K_a of hydrofluoric acid is very small.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 7.6 \times 10^{-4}$$

When a strong acid such as hydrochloric acid dissolves in water, almost 100 per cent reacts to form the hydronium and chloride ions:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

The K_a of a strong acid is very large. The reverse reaction only occurs to a very small extent. The conjugate base Cl^- is very weak and does not readily react in the reverse reaction. It is not necessary to use the equilibrium arrows for the reactions of strong acids as they effectively go to completion.

pH will determine the concentration of hydronium ions. For strong acids, the concentration of HCl molecules at equilibrium is negligible, so pH will give a direct measurement of the concentration of the acid. For weak acids, the pH does not give a direct measurement of the acid concentration.



STRONG AND WEAK ACIDS

View the animation about the difference in strong and weak acids.

The acid dissociation equilibrium constant is a measure of the strength of acids. Strong acids ionise completely in water; K_a is very large. Weak acids do not; K_a is small.

ACTIVITY 2.3

WEAK ACIDS

Aim

To show how 'weak' relates to the number of ions and molecules in a solution of a weak acid

You will need

- Calculator
- Computer with internet access

What to do

1. In a group of three or four students, discuss the problem.
2. Search on the internet for any monoprotic (monobasic) weak acid. Starting from its K_a value, calculate or find as much information as you need to show what is meant by 'weak' in weak acid.
3. Discussion can play a vital role as it can stimulate ideas. Spend about 10 minutes on the initial discussion.

What did you discover?

1. Write a brief account of what you did.
2. Prepare a short presentation aimed at 14–16-year-old students to be delivered to your class. Every group member should take part. Outline the problem and then present your solution.
3. Be prepared to answer questions and discuss what you discovered.

Table C2.3 Acidity constants, K_a, of some weak acids

Acid	Formula	K_a
Ammonium ion	NH_4^+	5.6×10^{-10}
Ethanoic	CH_3COOH	1.7×10^{-5}
Hydrocyanic	HCN	6.3×10^{-10}
Hydrofluoric	HF	7.6×10^{-4}
Lactic	$HC_3H_5O_3$	1.4×10^{-4}
Methanoic	HCOOH	1.8×10^{-4}

Acid dissociation equilibrium constants only apply when the acid is dissolved in water. They are temperature dependent and are usually quoted at 25°C.

Determining the K_a of two acids

The K_a of an acid can be determined by measuring the pH of the sample. Using HA to represent any acid and A^- to represent the conjugate base, the reaction of a weak acid with water can be represented as:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

And the equilibrium expression is:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

As $[A^-]$ must equal $[H_3O^+]$, then:

$$K_a = \frac{[H_3O^+]^2}{[HA]}$$

The following assumptions are made:

1. At equilibrium, [HA] is the same as the initial concentration; the weak acid only ionises to a small degree in water.
2. $[H_3O^+]$ produced by the self-ionisation of water is negligible and has no effect on the calculations.

WORKED EXAMPLE 2.4

A 0.1 M hypobromous (HOBr) acid has a pH of 4.80. Determine K_a for this acid.

Answer

$K_a = 2.5 \times 10^{-9}$

Logic

1 Write the equation for the ionisation of the acid.

$HOBr(aq) + H_2O(l) \rightleftharpoons H_3O^+ + OBr^-$

2 Write the expression for K_a.

$$K_a = \frac{[H_3O^+][OBr^-]}{[HOBr]}$$

3 Choose the correct formula and insert the numbers.

$pH = -\log[H_3O^+]$

$4.80 = -\log[H_3O^+]$

Therefore, $[H_3O^+] = 1.58 \times 10^{-5}$M

4 Insert numbers into the formula and calculate the answer.

$$K_a = \frac{[H_3O^+][OBr^-]}{[HOBr]}$$

$$= \frac{[H_3O^+]^2}{0.1}$$

$$= \frac{(1.58 \times 10^{-5})^2}{0.1} = 2.5 \times 10^{-9}$$

Try these yourself

a The pH of a 0.050 M solution of nitrous acid (HNO_2) is measured as 2.22. Determine the acid dissociation equilibrium constant.

b Determine the pH of a 0.2 M ethanoic acid solution ($K_a = 1.7 \times 10^{-5}$).

EXPERIMENT 2.4

DETERMINATION OF K_a OF A WEAK ACID

The acid dissociation equilibrium constant can be determined by measuring the pH of a solution with known molarity.

Aim

To determine K_a for the ionisation of the ammonium ion

Materials

- 0.10 M ammonium chloride solution
- 10 mL and 100 mL measuring cylinders
- Dropping pipette
- Stirring rod
- Distilled water
- 2 × 50 mL beakers
- pH meter or universal indicator solution

Complete the risk assessment box to show any risks associated with completing this experiment and ways to manage them.

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Ammonium chloride solution produces slightly toxic fumes on heating.	
Glassware	

Procedure

1. Place about 40 mL of the ammonium chloride solution in a 50 mL beaker. Measure and record its pH.
2. Use the 10 mL measuring cylinder to measure 1 mL of the ammonium chloride solution into the 100 mL measuring cylinder.
3. Add water to make it up to 100 mL. Remember to rinse the 10 mL measuring cylinder at least three times into the larger cylinder.
4. Pour about 40 mL of the diluted solution into a 50 mL beaker. Measure and record its pH.
5. Complete a table of your results.

Analysis of results

1. Write the expression for the ionisation of the ammonium ion.
2. For each solution calculate the K_a of the ammonium ion.

Discussion

1. What assumptions do you have to make to calculate K_a?
2. How close did you get to the expected value? What is the percentage error on your averaged result?

Conclusion

1. How would you improve the accuracy of the experiment?
2. What is the K_a of the ammonium ion according to your experiment?

Percentage ionisation

Percentage ionisation is the percentage of acid that has ionised in water. The general reaction for weak acids with water is:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

For each proton that is donated to water, one A^- ion is formed (provided the acid is monoprotic). By measuring the pH, the $[H_3O^+]$ can be determined and this is equal to $[A^-]$:

$$[A^-] = [H_3O^+]$$

This can then be used to calculate the percentage of the original acid that has been ionised. Note that [HA] here refers to the initial concentration and not the concentration at equilibrium:

$$\text{Percentage ionisation} = \frac{[A^-]}{[HA]} \times 100\%$$

Once the percentage ionisation is known, a more accurate calculation for K_a can be determined. Some weak acids may have significant ionisation (less than 100%), so the assumption that $[HA]_{initial} = [HA]_{equil}$ for K_a calculations may not be valid.

WORKED EXAMPLE 2.5

a Hydrofluoric acid (HF) reacts with water as shown by:

$HF(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \quad K_a = 6.8 \times 10^{-4}$

Determine the percentage ionisation of HF(aq) in a 0.1 M HF solution that was found to have a pH of 2.1.

b Determine the pH of a 0.01 M solution of HF ($K_a = 6.8 \times 10^{-4}$).

Answer

a Percentage ionisation = 8%

Logic

1 Choose correct formula and insert numbers.

The concentration of hydronium ions is:

$10^{-pH} = 10^{-2.1}$

$= 0.008\,mol\,L^{-1}$

2 Determine $[F^-]$.

Concentration of F^- is also $0.008\,mol\,L^{-1}$

3 Percentage ionisation of HF:

$$= \frac{[F^-]}{[HF]} \times \frac{100}{1}$$

$$= \frac{0.008}{0.1} \times \frac{100}{1}$$

$= 8\%$

b pH = 2.58

1 Choose correct formula and insert numbers.

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = 6.8 \times 10^{-4}$$

$$= \frac{[H_3O^+]^2}{[HF]}, \text{ as } [F^-] = [H_3O^+]$$

$[H_3O^+]^2 = 6.8 \times 10^{-4} \times [HF]$

$[H_3O^+] = \sqrt{(6.8 \times 10^{-4} \times 0.01)} = 2.6 \times 10^{-3}$

2 Determine pH.

$pH = -\log[H_3O^+]$

$= -\log(2.6 \times 10^{-3}) = 2.58$

Try these yourself

a A $0.1\,mol\,L^{-1}$ solution of methanoic acid (HCOOH) has a pH of 2.87 ($K_a = 1.8 \times 10^{-5}$). What is the:

- **i** concentration of hydronium ions?
- **ii** concentration of methanoate anions?
- **iii** percentage ionisation?

b Determine the pH of a 0.010 M methanoic acid solution.

INVESTIGATION 2.1

PERCENTAGE IONISATION OF A WEAK ACID

Both HCl and ethanoic acid will undergo ionisation reactions with water, producing hydrogen ions and chloride ions (Cl^-) or ethanoate ions (CH_3COO^-). Although the two reactions are similar, there is a significant difference in the extent to which they occur.

The strong acid HCl ionises completely in water. The pH can be used to directly measure the concentration.

The pH of a 1.0M ethanoic acid can be readily determined. The pH will measure the concentration of hydronium ions. This can then be used to determine the K_a value of ethanoic acid. This calculation assumes that the percentage ionisation is low. If the percentage ionisation is not low, then there will be a large error in the calculated K_a.

What is your aim?

To determine the percentage ionisation of a 1.0M ethanoic acid solution

What will you need?

- 1.0M hydrochloric acid
- 1.0M ethanoic acid
- Distilled water
- An indicator such as thymol blue or methyl red
- 1 mL plastic pipettes
- Glass rod
- pH meter
- Test tubes and test-tube rack
- 10mL and 100mL measuring cylinders
- Marking pen
- Calculator

What are the risks?

Complete the risk assessment box to show any risks associated with completing this investigation and ways to manage them.

What are the risks in doing this investigation?	How can you manage these risks to stay safe?
1.0 M hydrochloric acid	
Glassware	
Indicator	

How will you carry out your investigation?

1. Working as a group, discuss how you could determine the percentage ionisation of ethanoic acid by using the items provided.
2. Get your teacher to check your method and risk analysis before starting the practical activity.

What results will you collect?

What will you record: the pH or the colour? Justify your decision.

What have you found?

Calculate the percentage of ethanoic acid that has been ionised, assuming the hydrochloric acid is completely ionised.

What do you conclude?

1. Given the results of this experiment, how does the value of the equilibrium constant, K, for the ionisation of HCl compare with the value of K for the ionisation of CH_3COOH?
2. Is the error in determining the K_a for ethanoic acid large?

Taking it further

Measure the electrical conductivity of each of the solutions in the test tubes and account for the results.

2.5 K_a of polyprotic acids

A separate equation can be written for each step of the ionisation of a polyprotic acid. Each step has its own equilibrium expression and K_a. These are generally labelled K_{a1}, K_{a2} and so on, and the first K_a is usually the largest. Sulfuric acid is a diprotic acid – it can release two protons, the first being donated very easily to water. Sulfuric acid (H_2SO_4) is a strong acid with a conjugate base, HSO_4^-.

$$H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq) \quad K_{a1} = 10^9$$

K_a for the strong acid is very large. The second reaction is:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq) \; K_{a2} = 10^{-2}$$

The conjugate base HSO_4^- is now donating a proton and acting as a weak acid by reacting with water to form SO_4^{2-}. The weaker a weak acid, the stronger is its conjugate base, so the reverse reaction occurs to higher degree. The species HSO_4^- is amphiprotic. In a solution of sulfuric acid, the main species present are HSO_4^-, H_3O^+ and water.

Diprotic weak acids such as sulfurous acid (H_2SO_3) have two ionisable protons:

$$H_2SO_3^-(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \; K_{a1} = 1.7 \times 10^{-2}$$

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \quad K_{a2} = 6.4 \times 10^{-8}$$

Sulfurous acid is a weak acid and in the first reaction it is in equilibrium with the conjugate base. While K_{a1} is bigger than K_{a2}, all three species would be expected to be present in an aqueous solution of sulfurous acid.

To see an example of polyprotic acids, refer to Context 1, 'Wine', page 20.

QUESTION SET 2.3

Remembering

1 Write the acid dissociation equilibrium expression for the following acids in water.
   - a Hypobromous, HOBr
   - b Hydrocyanic, HCN
   - c Ammonium ion, NH_4^+

2 What are the differences between a strong and weak acid? Provide three examples of strong acids and three examples of weak acids.

3 Write the reactions of the following substances with:
   - a hydrochloric acid.
   - b sodium hydroxide.

   If the reaction does not occur, then state 'No reaction'.
     - i HS^-
     - ii HSO_3^-
     - iii HCOOH
     - iv $H_2NCH(CH_3)COOH$ (alanine amino acid)

Understanding

4 Malic acid is a diprotic acid, commonly found in fruit. Write the two acid dissociation equilibrium expressions for the ionisation of this acid in water. Which K_a is larger? Explain.

5 Phenol (C_6H_5OH) was used as an antiseptic for wounds and in chamomile lotions for skin irritations. It is a weak monoprotic acid with a K_a of 1.05×10^{-10}. Calculate the pH of a 3.5×10^{-3}M solution of phenol and determine the percentage ionisation.

Analysing

6 Consider the equation: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
- a Calculate K_a for the ionisation of CH_3COOH to its conjugate base CH_3COO^-.
- b Calculate K_b for $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$.
- c Show how $K_w = K_a \times K_b$.
- d Explain why $K_w = K_a \times K_b$ can be used to calculate the pH for an alkaline solution.

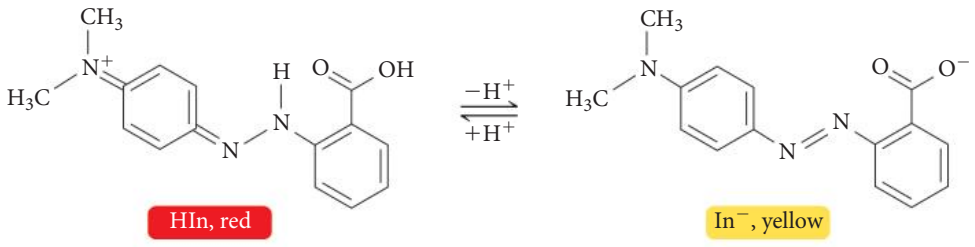
7 a Write an equation showing the equilibrium that occurs when ethanoic acid ionises in water.
- b The K_a for ethanoic acid is 1.74×10^{-5} mol L^{-1}. What is the pH of a 0.4 M solution?

2.6 Indicators

Indicators are molecular substances that are used because they change colour depending on the pH of the solution. An indicator is a weak acid and its conjugate base pair. The weak acid has a different colour from its conjugate base. Table C2.4 lists some common acid–base indicators and the pH ranges over which they change colour and their K_a values.

Table C2.4 Acid–base indicators

Indicator	pH range	Colour change		K_a
		Acid	Base	
Thymol blue	1.2–2.8	Red	Yellow	2×10^{-2}
Methyl orange	3.1–4.4	Red	Yellow	2×10^{-4}
Bromophenol blue	3.0–4.6	Yellow	Blue	6×10^{-5}
Methyl red	4.2–6.3	Red	Yellow	8×10^{-6}
Litmus	5.0–8.0	Red	Blue	1×10^{-7}
Bromothymol blue	6.0–7.6	Yellow	Blue	1×10^{-7}
Phenol red	6.8–8.4	Yellow	Red	1×10^{-8}
Phenolphthalein	8.3–10.0	Colourless	Red	5×10^{-10}



◀ **Figure C2.11** Methyl red indicator has a bright red colour (HIn) in acidic solution, which changes to the yellow conjugate base (In^-).

When methyl red is added to an acidic solution in which the concentration of H_3O^+ is high, the red form predominates because the system attempts to partially oppose the increase in H_3O^+. By favouring the formation of HIn, the amount of hydronium ions is reduced. When methyl red is added to a basic solution in which the concentration of H_3O^+ is low, the forward reaction is favoured and the yellow form predominates. The system attempts to partially oppose the decrease in H_3O^+ by shifting the reaction forward to produce more H_3O^+ ions.

$$HIn + H_2O \rightleftharpoons In^- + H_3O^+ \quad K_a = 8 \times 10^{-6}$$

Red Yellow



Figure C2.12 ▶ Common indicators in acidic and alkaline solutions

Andrew Lambert Photography/Science Photo Library

Mathematics can be used to show this relationship. When methyl red is added to a 0.01 M HCl solution, the pH is 2. Substituting this into the expression for K_a gives:

$$K_a = \frac{[In^-][H_3O^+]}{[HIn]}$$
$$= \frac{[In^-] \times 10^{-2}}{[HIn]}$$
$$= 8 \times 10^{-6}$$

Therefore, $\frac{[In^-]}{[HIn]} = 8 \times 10^{-4}$ $[HIn] \gg [In^-]$

[HIn] is much larger than $[In^-]$ and the solution is red. Most of the indicator is present as HIn(aq).

When methyl red is added to a solution of 0.01 M NaOH, the pH is 12 and the concentration of H_3O^+ is 10^{-12}.

Substituting this into the same expression for K_a gives the following for the basic solution.

$$K_a = \frac{[In^-][H_3O^+]}{[HIn]}$$
$$= \frac{[In^-] \times 10^{-12}}{[HIn]}$$
$$= 8 \times 10^{-6}$$

Therefore, $\frac{[In^-]}{[HIn]} = 8 \times 10^{-6}$, $[HIn] \ll [In^-]$

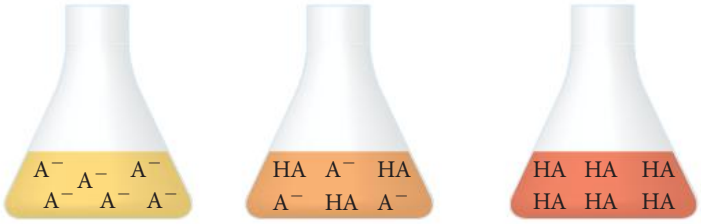
[HIn] is much smaller than $[In^-]$ and the solution is yellow.

When the concentration of [HIn] = $[In^-]$, the ratio $\frac{[HIn]}{[In^-]} = 1$.

So $[H_3O^+] = K_a$. Both forms are present in the same ratio and the colour is between the two forms and the solution is orange. This occurs over a range of pH values as shown in Table C2.4.

Acid–base indicators are a conjugate pair with at least one intensely coloured. In titrations the end point is when the colour changes. K_a at this point equals $[H_3O^+]$ as $\frac{[A^-]}{[HA]} = 1$.

Indicators are chosen so that the colour change occurs at or near the equivalence point of the reaction. In this way, the end point is close to the equivalence point and errors are reduced.



Indicator in base

Most HA molecules have donated H^+ to the base so mainly A^- is present.

Indicator in water

Both HA and A^- are present.

Indicator in acid

Most A^- ions have accepted H^+ from the acid, so mainly HA is present.

◀ **Figure C2.13**
How an acid–base indicator works

EXPERIMENT 2.5

SPECTROSCOPIC DETERMINATION OF K_a OF AN INDICATOR

Indicators are weak acids that change colour at different pH values. By using a buffer solution (buffers resists changes in pH over a small range), the K_a of an indicator can be determined by spectroscopy.

Weak acids such as bromothymol blue ionise in water as shown:

$HIn + H_2O \rightleftharpoons In^- + H_3O^+$

Yellow Blue

Acid form Base form

The acid dissociation equilibrium expression is:

$$K_a = \frac{[In^-][H_3O^+]}{[HIn]}$$

To determine K_a, you need both the pH and the concentration of the acid and conjugate base. A pH measurement will indicate the concentration of hydronium ions. As indicators are coloured, it is possible to use UV–visible spectroscopy to determine the concentration of the weak acid and its conjugate base. In this case, the wavelengths have been predetermined to provide the most accurate measurement of the concentrations of both.



bfesser/Wikimedia Commons/Public Domain

▲ **Figure C2.14**
Bromothymol blue indicator is yellow in acidic solutions and blue in basic solutions.

The acid form HIn absorbs best at 450 nm.

The basic form In^- absorbs best at 550 nm.

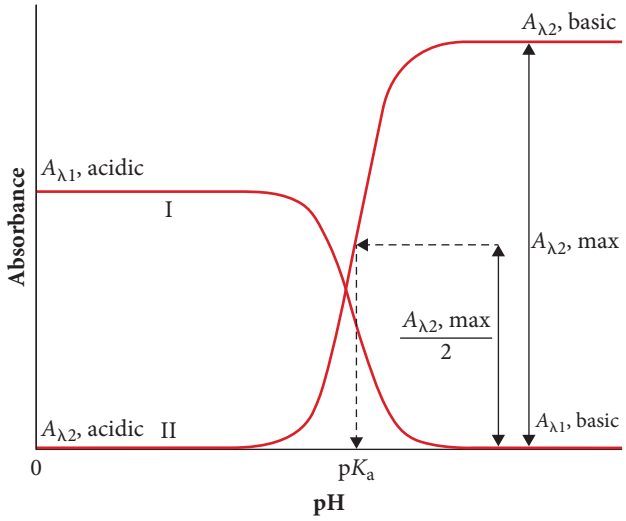
Which form is more prevalent will depend upon the pH. So, as the pH changes, the absorption at the two wavelengths will change.

It is known that:

$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$

$$pH = pK_a \text{ when } \frac{[In^-]}{[HIn]} = 1$$

The absorbance is measured for a series of samples and is plotted against the pH. The concentrations of both forms are equal at the pH where the absorbance for both is half the maximum value, as shown in Figure C2.15.



◀ **Figure C2.15**
Absorbance as a function of pH for the indicator.
I: Measurement at the wavelength (λ) at which HIn absorbs radiation. II: Measurement at the wavelength that In^- absorbs radiation



To learn about UV–visible spectroscopy, refer to Chemistry section 8.6, page 397.

Aim

To determine the K_a of bromothymol blue (0.1% solution)

Materials

- 0.1% bromothymol blue (0.1% in 20% ethanol)
- Concentrated HCl
- 0.1 M KH_2PO_4
- 0.1 M Na_2HPO_4
- 4 M sodium hydroxide solution
- Spectrometer
- 1 mL pipette
- 5 mL pipette
- 12 × 25 mL volumetric flasks
- 10 mL measuring cylinder
- Cuvettes

Complete the risk assessment box to show any risks associated with completing this experiment and ways to manage them.

What are the risks in doing this experiment?	How can you manage these risks to stay safe?

Procedure

1. Add 1.00 mL of bromothymol blue to each of two labelled 25 mL standard flasks.
2. Add 5 mL of distilled or deionised water and 4 drops of concentrated hydrochloric acid to one of the flasks. Make up to 25 mL. This solution should have a pH of around 1.
3. To the second flask, add 12 drops of 4 M sodium hydroxide solution and fill the flask to the mark with water. The solution should have a pH of around 13.
4. Prepare a series of 25 mL volumetric flasks prepared as shown in the table and make up to the mark. Ensure that the flasks are labelled.

Buffer sample	Vol. 0.1% bromothymol blue (mL)	Vol. 0.1 M KH_2PO_4 (mL)	Vol. 0.1 M Na_2HPO_4 (mL)	Vol. H_2O (mL)	pH	450*A*	550*A*
1	1.0	5.0	0.0	19.0			
2	1.0	5.0	1.0	18.0			
3	1.0	10.0	5.0	9.0			
4	1.0	5.0	10.0	9.0			
5	1.0	1.0	5.0	18.0			
6	1.0	1.0	10.0	13.0			
7	1.0	0.0	5.0	19.0			
8	1.0	HCl standard					
9	1.0	NaOH standard					

5 Read the pH of each sample.

Results

1 Record the pH of each sample.
2 Using water as a blank record the absorbance for each sample at the wavelength of 450nm.
3 Repeat step 2 for each sample at the 550nm wavelength.

Analysis of results

Plot the absorbance (*y* axis) against the pH for the solution at each of the two wavelengths.

Discussion

1 Why are two different wavelengths used?
2 Why must there be a wide range of samples tested?
3 Why can't the measurement of the pH of the solution be used directly to measure the K_a?
4 Why is the K_a at the junction where the two graphs meet?
5 What difficulties did you encounter?

Conclusion

Determine the K_a for bromothymol blue.

Taking it further

Develop a procedure to measure the K_a of another indicator.

Buffers

Buffers are solutions that can maintain a pH within a certain range despite addition of an acid or a base. These chemicals play an important role in maintaining the pH of the body to within a narrow range. Buffers enable enzymes to continue to function effectively by protecting them from being denatured due to changes in acidity.

Buffers are solutions in which both a weak acid and its conjugate base are present, or when a weak base and its conjugate acid are present. An example is a solution of carbonic acid and sodium hydrogen carbonate H_2CO_3/HCO_3^-.

The pH of a buffer is determined by the:

- equilibrium constant K_a of the weak acid
- ratio of weak base $[A^-]$ to weak acid [HA] in solution.

If a buffer has more acid than base, more H^+ ions are present and the pH is lower. When the concentrations of A^- and HA are equal, $[H^+]$ is equal to K_a.

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

If a strong acid is added, the extra H_3O^+ pushes the equilibrium reaction to the left to partially reduce the concentration of H_3O^+. The pH increases to near the original value. Addition of a strong base (OH^-) will result in the added OH^- reacting with the H_3O^+.



To see an example of buffering in the environment, refer to Context 5, 'Aquatic chemistry', page 119.

The system will try to oppose this change and move to produce more H_3O^+, shifting to the right. The pH is decreased to near the original value.

The pH is maintained by manipulating the proportion of weak base (A^-) and weak acid (HA) in solution. As long as $[A^-]/[HA]$ is between 1/10 and 10, the pH is within is 1 unit and the solution is therefore buffered.

Blood chemistry

The pH of many biological systems are maintained within narrow ranges by buffers. The pH range for human blood is 7.35–7.45. The main buffer system in blood is the carbonic acid/hydrogen carbonate ion system:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

If blood becomes too acidic, then the reverse reaction occurs to reduce the excess H_3O^+. If the blood becomes too basic, then the forward reaction occurs to increase the H_3O^+ to neutralise the excess base.

This buffer is also involved in the transport of the waste carbon dioxide from the cells. Carbon dioxide is a clear odourless gas, which is produced in every cell in the body. The carbon dioxide has to dissolve in blood, which is an aqueous medium in accordance to the reaction:

$$CO_2(g) \rightleftharpoons CO_2(aq) \quad (1)$$

In enzyme-catalysed reactions, the dissolved carbon dioxide then reacts with water in the blood to form carbonic acid as shown in reactions (2) and (3). The majority of the carbon dioxide is transported in the blood to the lungs as the hydrogen carbonate ion.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \quad (2)$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \quad (3)$$

OXYGEN MYSTERY

Visit this website to read how scientists finally solved the mystery of how marine mammals hold their breath.



WaterFrame/Alamy

Figure C2.16 ▲
Animals such as Australian seals have a high tolerance for carbon dioxide in their blood. This, in part, allows them to dive for extended periods of time.

The acidity of the blood increases as more carbon dioxide is dissolved.

Once the blood reaches the lungs, the reverse series of reactions occurs with the carbon dioxide gas diffusing into the air space in the lungs. Carbon dioxide is breathed out. The concentration of carbon dioxide in the lungs is lower than in blood. The first reaction (1) proceeds to the left, which reduces the concentration of $CO_2(aq)$. Reducing $[CO_2(aq)]$ has the effect of pushing reaction (2) to the left. This reduces $[H_2CO_3]$ so that reaction (3) is also pushed to the left. Overall, $[H_3O^+]$ decreases. The amount of CO_2 in the blood is maintained within a narrow band, which helps prevent blood from becoming too acidic.

Sea-diving animals such as whales, seals and dolphins can stay under water for more than an hour. Other adaptations these organisms have include a higher tolerance for carbon dioxide in their blood compared to humans. Humans can generally only hold their breath for a couple of minutes. It is the high level of carbon dioxide, not the low level of oxygen, that causes the breathing reflex when holding one's breath.

With increasing carbon dioxide levels in the atmosphere, there is a major concern that the oceans are being acidified. In ocean waters, carbon dioxide is found in higher concentrations than other non-polar gases as it reacts with water. The changes in pH at these levels are significant and are altering the thickness of shells and the ability of organisms to take up calcium. Reactions (1)–(3) can also explain how the ocean is becoming acidified.

WOW

Not for sale at any price

Carbonic acid cannot be purchased from any laboratory supply or chemical manufacturer, but not because it is dangerous. It was thought to be too unstable to isolate and directly detect. Since it was discovered in 1757 by Dr Joseph Black, many uses of this acid have been developed. Although the acid could not be seen, scientists used their knowledge of acids to predict its reactions and behaviour.

In 2010, Austrian researchers isolated this acid. They produced carbonic acid at very low temperatures by a series of acid–base reactions. They then warmed the system to −30°C, trapped the molecules in argon and cooled it again. With the use of infrared spectroscopy, they have shown that carbonic acid exists in three forms. Astronomers have a great interest in this as it allows them to show that carbonic acid exists in the tails of comets and on Mars.



For more information about infrared spectroscopy, refer to Chemistry section 8.5, page 392.

QUESTION SET 2.4

Remembering

1 Define 'buffer' and give an example.

2 What are indicators?

Understanding

3 An aqueous solution of ethanoic acid/ethanoate ion can act as a buffer.

- **a** What is a buffer solution?
- **b** Use Le Chatelier's principle to explain what happens when a small amount of the following are added.
  - **i** HCl
  - **ii** NaOH

4 Bromophenol blue is a common acid–base indicator. The reaction of bromophenol blue with water is:

$$HBrb(aq) + H_2O(l) \rightleftharpoons Brb^-(aq) + H_3O^+(aq) \quad K_a = 6.31 \times 10^{-5}$$

- **a** Write an expression for the acidity constant of bromophenol blue.
- **b** Determine the pH of the endpoint for this indicator.

Applying

5 The pH of seawater has fallen from 8.2 to 8.1 over the last 200 years.

- **a** Calculate the percentage change in $[H_3O^+]$.

One main concern is the ability of marine organisms to build calcium carbonate structures such as shells. Sea water is basic because it is naturally saturated with carbonate ion (CO_3^{2-}), which is a base.

- **b** Explain how this base is buffering the increase in acidity and how this is also causing the reduction of calcium carbonate-based structures such as shells.

Use the following series of reactions:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O(aq) \quad K_a = 4.5 \times 10^{-7}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq) \quad K_a = 4.7 \times 10^{-11}$$

6 The indicator phenolphthalein (HP) changes from pink in basic solution to clear in acidic solution. This indicator has an acid dissociation equilibrium constant of 5×10^{-10}. The reaction in water is:

$$HP(aq) + H_2O(l) \rightleftharpoons P^-(aq) + H_3O^+(aq)$$

Determine the magnitude of the ratio $[P^-]/[HP]$ for phenolphthalein and the dominant species present in solutions of pH:

- **a** 6
- **b** 11

Analysing

7 It is a common practice for doctors to inject a solution of sodium hydrogen carbonate directly into the heart of a patient who has suffered cardiac arrest. Under cardiac arrest the heart is not supplied with blood and carbon dioxide builds up. Death may follow. Explain how the hydrogen carbonate might be of benefit to the patient.

CHAPTER CHECKLIST

You should know:

- acids are substances that can act as proton (hydrogen ion) donors and can be classified as monoprotic or polyprotic depending on the number of protons donated by each molecule of the acid
- the Brønsted–Lowry definition of acids is a broader definition than the earlier definitions of Davy and Arrhenius. This definition explains how many more substances can act as a base: bases are proton acceptors
- the acid donates a proton to form the conjugate base. A base accepts a proton to form the conjugate acid
- amphiprotic salts, buffer systems, indicators are all conjugate acid–base pairs
- acid–base indicators are weak acids or bases for which the acidic form is a different colour from the basic form
- the Brønsted–Lowry definition explains that the concentration of hydronium ions is a measure of acidity
- the pH scale is based upon the self-ionisation of water (K_w)
- concentration of a solution refers to amount in a certain volume, such as molarity, v/v%, w/w% and ppm
- pH can be used for determining the concentration of a strong acid or a strong base. pH is a measure of the hydronium ions from which the concentration of hydroxide ions in a solution can be calculated
- if an acid reacts with a different base (not the conjugate base and not water), it will always react 100%. This means that the same calculations are used to determine the amount needed for neutralisation for both weak and strong acids
- strength of an acid refers to the ability of the acid to donate a proton in water
- strong acids completely ionise in water and have a large equilibrium constant (K_a). Weak acids have a small K_a and do not as readily donate their protons
- Le Chatelier's principle can be applied to weak acids including buffers, and indicators. It explains how these work.

You should be able to:

- design investigations including the procedure to determine the percentage ionisation of a weak acid
- represent acid–base reactions as equilibrium equations, determining the expressions for the acid dissociation equilibrium constant K_a, for both monoprotic and polyprotic acids
- recognise conjugate acid and base pairs
- calculate the pH of solutions of strong acids and bases and, by using K_a values, calculate the pH of weak acids and bases
- calculate the percentage ionisation for a weak acid given the pH and K_a
- predict the pH of a weak acid given the concentration and K_a
- predict, given the K_a, the pH at which the indicator will change colour
- represent ionisation, dissociation and the reactions of weak acids and bases using chemical equations.

CHAPTER GLOSSARY

acid dissociation equilibrium constant (K_a) the equilibrium expression of a weak acid

amphiprotic a substance that can gain or lose a hydrogen ion to act as an acid or a base

conjugate acid (of a base) the acid that is formed when a base accepts a proton from an acid

conjugate base (of an acid) the base that is formed when an acid donates a proton to a base

conjugate pairs compounds that differ by one proton (H^+); for example, HCl/Cl^-

diprotic a substance that can donate two protons to a base

dissociation reaction a reaction in which an ionic substance separates in a solution

hydronium ion the ion that forms when a proton is donated to a water molecule (H_3O^+)

ionisation reaction a chemical reaction when an uncharged molecule becomes an ion

monoprotic a substance that can donate one proton to a base

polyprotic a substance that can donate more than one proton to a base

percentage ionisation the percentage of the acid molecules that have ionised in water

self-ionisation constant (K_w) the equilibrium expression that shows water ionising into two ions

strong acid an acid that readily donates a proton to water; K_a is large

triprotic a substance that can donate three protons to a base

weak acid an acid in which only a small proportion of the molecules will donate their proton; the K_a is small

CHAPTER REVIEW QUESTIONS

Remembering

1 State the names and formulas of two polyprotic acids.

2 A 50 mL solution of pH 5 is mixed with a 50 mL solution of pH 3. Explain why the pH is closer to 3 than to 4.

3 Why is the conductivity of a solution at pH 6 similar to that of a solution at pH 8?

4 What makes a buffer solution? What would be a suitable substance to mix with methanoic acid to make a buffer?

5 Give the expression for the acid ionisation constant for:

- **a** hydrofluoric acid.
- **b** phosphoric acid.
- **c** benzoic acid (C_6H_5COOH).

6 Write an expression for K_a for methanoic acid in aqueous solution. Explain why this can be used to define a weak acid.

7 Why do acids such as malic and citric acid have two K_a values?

8 Two acids have the following values for K_a.

- Acid A: 6.32×10^{-5}
- Acid B: 1.50×10^{-4}

Two different acids have the following pH values.

- Acid C: 3.24
- Acid D: 5.66

Rank these acids from weakest to strongest. The concentration of each acid is 1 M.

Understanding

9 Calculate the pH of the following solutions.

- **a** 0.050 M HCl(aq)
- **b** 0.020 M NaOH(aq)
- **c** 40.0 mL of 0.200 M hydrochloric acid solution reacts with 20.0 mL of a 0.100 M sodium hydroxide solution. Calculate the pH of the resulting solution.

10 A 0.25 M solution of sodium hydrogen sulfate has a pH of 1.31 at 25°C. Calculate the ionisation constant for the hydrogen sulfate ion.

11 Given that the pH of water at 100°C is 6.14, calculate K_w at this temperature.

12 What mass of sodium hydroxide must be dissolved in water to produce 750 mL of solution with pH 13?

13 Write all the equilibrium expressions for phosphoric acid. The K_a values are 7.5×10^{3}, 6.2×10^{-8} and 2.2×10^{-13}. Explain the trend in the size of the K_a values.

14 **a** Write the equilibrium expression for citric acid as it reacts with water.

- **b** Explain the effect of the addition of acid on a solution of citric acid. How is the pH affected?
- **c** Explain what occurs when the citric acid solution is diluted by a factor of 10. How could this be experimentally determined?

15 A student is investigating an equilibrium mixture produced by reacting methanoic acid (HCOOH) with water. She finds that the pH of the solution is 2.40 and the concentration of HCOOH is 0.10 M. Calculate the K_a of methanoic acid.

Applying

16 **a** Write the expression for the reaction of hydrogen carbonate with water. Label the two conjugate acid and base pairs.

b Calculate the pH of a solution that contains 0.25 mol L^{-1} of sodium hydrogen carbonate and 0.4 mol L^{-1} of sodium carbonate, given that the $K_a = 4.7 \times 10^{-11}$. What general name is given to solutions like this example?

17 Boric acid (H_3BO_3) is a weak acid. Its conjugate base, the borate ion, exists as $B(OH)_4^-$.

A solution of pure sodium borate, $NaB(OH)_4$, is prepared in water at 25°C. The borate ion dissociates according to the equation:

$$B(OH)_4^-(aq) \rightleftharpoons OH^-(aq) + H_3BO_3(aq)$$

a Give the equilibrium expression for this reaction.

At equilibrium, the concentration of $B(OH)_4^-$ was exactly 0.1 M and the pH was determined to be 11.11.

b Calculate the hydrogen ion and hydroxide ion concentrations in the solution.

c Calculate the H_3BO_3 concentration.

d Calculate the K_a of boric acid.

18 Describe how the ionisation constant of a weak acid is determined.

Analysing

19 Hydrogen cyanide gas is highly toxic. It dissolves in water to form a weak acid.

The reaction is: $HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$

The acidity constant is 6.3×10^{-10}.

a Write the expression for the acidity constant.

b Calculate the pH of a solution of HCN of concentration 0.00010 mol L^{-1}.

c Calculate the percentage ionisation of the HCN solution at this concentration.

d The mining industry uses solutions of HCN to extract gold. Explain why the solutions are always kept above pH 7.

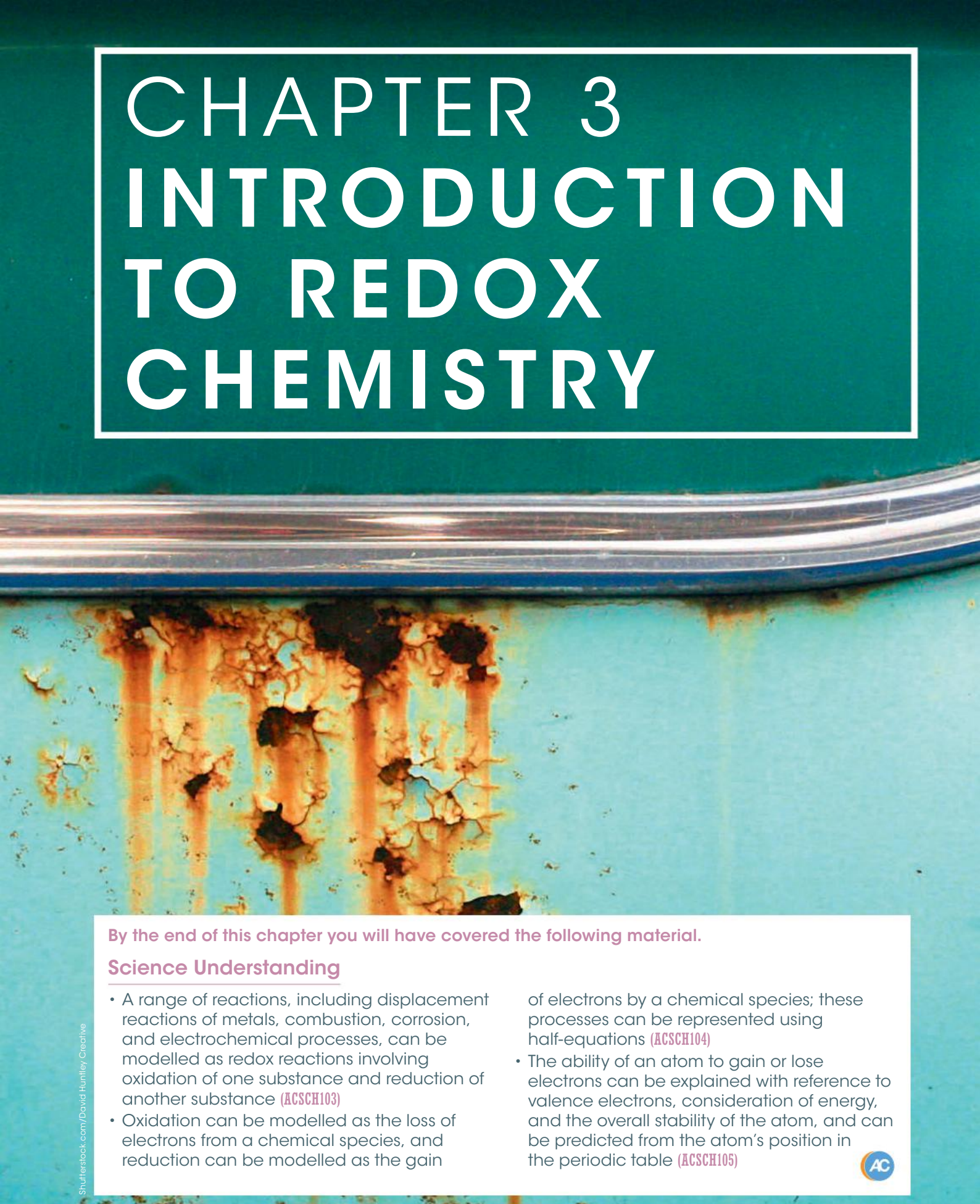
20 Why is bromothymol blue actually green at a pH of 7?

21 Explain how buffers can keep the pH within a narrow range despite the addition of small amounts of acids.

Reflecting

22 Use examples from nature to explain why competing equilibria can be both beneficial and harmful.

CHAPTER 3 INTRODUCTION TO REDOX CHEMISTRY



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By the end of this chapter you will have covered the following material.

Science Understanding

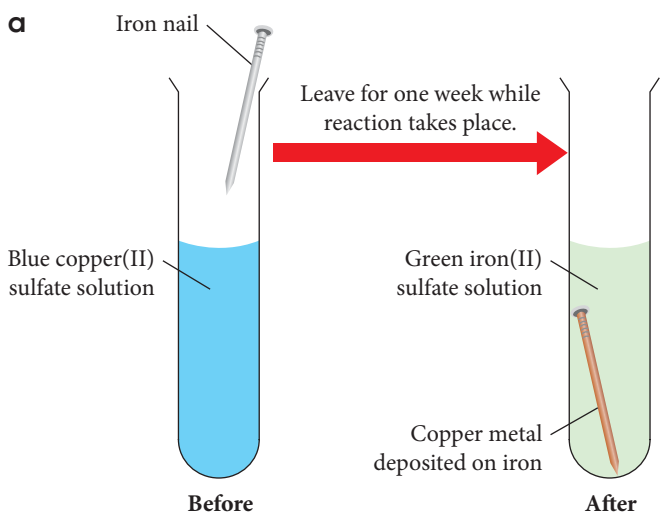
- A range of reactions, including displacement reactions of metals, combustion, corrosion, and electrochemical processes, can be modelled as redox reactions involving oxidation of one substance and reduction of another substance (ACSCH103)
- Oxidation can be modelled as the loss of electrons from a chemical species, and reduction can be modelled as the gain of electrons by a chemical species; these processes can be represented using half-equations (ACSCH104)
- The ability of an atom to gain or lose electrons can be explained with reference to valence electrons, consideration of energy, and the overall stability of the atom, and can be predicted from the atom's position in the periodic table (ACSCH105)

3.1 Introduction

Chemical reactions can be classified in many different ways. In Years 9 and 10, you learnt that chemical reactions can be classified as:

- single-displacement reactions
- double-displacement reactions
- synthesis reactions
- decomposition reactions
- combustion reactions.

However, reactions can also be grouped in other ways. Some reactions can be classified as **redox reactions**; these include displacement reactions of metals, combustion, corrosion and other electrochemical processes.





Kesu/Shutterstock.com



JC Photo/Shutterstock.com

Figure C3.1 ▶ a) Displacement reaction of metals; b) burning – combustion reaction; c) rusting – corrosion reaction

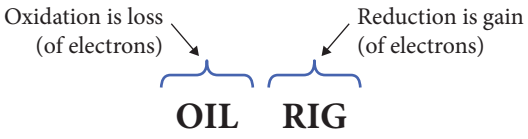
3.2 Redox reactions

Redox reactions are oxidation and reduction reactions and involve the transfer of electrons. New substances are formed when one species loses electrons and another species gains these electrons. **Oxidation** involves the loss of electrons, while **reduction** involves the gain of electrons. One cannot occur without the other. A substance cannot lose electrons unless there is another substance present to accept the electrons.



◀ **Figure C3.2**
Unpacking redox

Oxidation is the loss of electrons. Reduction is the gain of electrons.



◀ **Figure C3.3**
Mnemonic for redox reactions

In *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 4, you conducted experiments to rank some metals from most reactive to least reactive. This is redox chemistry. The metal that was most reactive in these experiments, calcium, was the metal that most readily lost electrons to form its ion, Ca^{2+}. It was so reactive that it reacted with water. The other metals tested – magnesium, zinc, iron and copper – were less reactive; they did not react with water. Pieces of each of the metals that did not react with water were placed into test tubes containing 1 mol L^{-1} hydrochloric acid. If they still did not react, they were placed into test tubes containing 4 mol L^{-1} hydrochloric acid. The copper did not react with the water or any of the acid solutions.

The reactivity series for these metals was:

$$Ca > Mg > Zn > Fe > Cu$$

Magnesium reacted with the 1 mol L^{-1} hydrochloric acid according to the equation:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

This reaction can also be written as an ionic equation:

$$Mg(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq) + H_2(g)$$

This equation indicates that the chloride ions (Cl^-) are spectator ions – they do not take part in the chemical reaction. Hence, the reaction can be rewritten as a net ionic equation, which shows only the species that are changing during the chemical reaction:

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

This equation shows that the magnesium metal has been oxidised – it has lost electrons to form magnesium ions. The hydrogen ions have been reduced – they have gained electrons to form hydrogen gas. This reaction can be split to show these two parts –called **half-equations**, since each of them shows half of what is occurring in the chemical reaction.

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ Oxidation

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ Reduction

The electrons have been transferred from the magnesium metal to the hydrogen ions.

To revise reactivity of metals, refer to Nelson Chemistry Units 1 & 2 for the Australian Curriculum, *Chapter 4.*



To see how metal activity is related to metal extraction processes, refer to Context 2, 'Chemical industry', page 37.



For information about the development of our knowledge of reactivity and oxidation and reduction reactions, refer to Context 3, 'Alternative sources of energy', page 60.

Since the magnesium metal lost electrons and caused the hydrogen ions to gain them, the magnesium metal is called the **reductant** or **reducing agent** since it caused another species to be reduced. The hydrogen ions gained electrons and caused the magnesium metal to lose them. So it is called the **oxidant** or **oxidising agent** since it caused another species to be oxidised.

A reductant or reducing agent causes another species to be reduced and hence is itself oxidised.
An oxidant or oxidising agent causes another species to be oxidised and hence is itself reduced.

Metal displacement reactions

Metal displacement reactions are examples of redox reactions. A metal displacement reaction occurs when a metal is added to an ionic solution containing the ion of another metal. The anion in this solution is a spectator ion, as it does not take part in the chemical reaction. The general equation for a metal displacement reaction is written as:

$$AB(aq) + C(s) \rightarrow CB(aq) + A(s)$$

EXPERIMENT 3.1

METAL DISPLACEMENT REACTIONS

You will use combinations of metals and solutions of these metals to rank the metals from most reactive to least reactive; that is, most easily oxidised to least likely to oxidise.

Aim

To rank the metals from most easily oxidised to least likely to be oxidised

Materials

- 100 mL of 1 mol L^{-1} $AgNO_3$
- 100 mL of 1 mol L^{-1} $CuSO_4$
- 100 mL of 1 mol L^{-1} $MgSO_4$
- 100 mL of 1 mol L^{-1} acidified $FeSO_4$
- 100 mL of 1 mol L^{-1} $ZnSO_4$
- 100 mL of 1 mol L^{-1} NaCl
- 5 strips of copper metal
- 5 strips of magnesium ribbon
- 5 ungalvanised iron nails
- 5 strips of zinc metal
- 4 × 100 mL beakers
- Waste bottles for heavy metals
- 7 cm × 7 cm piece of sandpaper

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Silver nitrate can stain skin.	Be careful when pouring from the bottle to the beaker. Wipe up drips with paper towelling or a sponge.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Use the sandpaper to clean all of the pieces of metal.
2. Pour 25 mL of 1 mol L^{-1} $AgNO_3$ into four separate beakers.
3. Place one piece of each metal into different beakers.
4. Record your observations.

5 Repeat for all of the other combinations of metals and solutions. You do not need to place metals with their corresponding solution; for example, you do not need to place magnesium into the $MgSO_4$ solution.
6 Record your observations for all combinations.
7 Dispose of copper(II) sulfate and silver nitrate by pouring them into the heavy metals waste bottle. Do not pour them down the drain.

Results

1 Draw a table where the metals are across the top and the solutions are down the side.
2 Record your results in the table, using either words or photos. Remember that no reaction is also a result.

Analysis of results

1 Identify the combinations of metals and solutions where chemical reactions occurred.
2 Which metal was most reactive?
3 Which metal was least reactive?
4 Explain why $AgNO_3$ and NaCl were included in the experiment. Compare the ability of silver ions and sodium ions to oxidise with reference to your observations.

Discussion

1 Identify the metal that was most easily oxidised and relate it to its reactivity.
2 Identify the metal that was least readily oxidised and relate it to its reactivity.

WORKED EXAMPLE 3.1

Copper deposited on the iron nail in Experiment 3.1. The copper ions were reduced to form copper metal while the iron metal was oxidised to form iron(II) ions. For this reaction:

a write the overall balanced equation.
b write the net ionic equation.
c write the two half-equations.
d identify the oxidant and the reductant.

Answers

a $CuSO_4(aq) + Fe(s) \rightarrow FeSO_4(aq) + Cu(s)$
b $Cu^{2+}(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + Cu(s)$
c $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
d Oxidant is $Cu^{2+}(aq)$
Reductant is Fe(s).

Try these yourself

Choose two other reactions that occurred in Experiment 3.1. For each reaction:

a write the overall balanced equation.
b write the net ionic equation.
c write the two half-equations.
d identify the oxidant and the reductant.

WOW

Naming ions

In 1919, Alfred Stock suggested that the naming of metal ions should be simplified to identify their valency. Previously, Fe^{2+} was known as the ferrous ion and Cu^{2+} was known as the cupric ion. Stock simplified these to iron(II) and copper(II). This is called the Stock nomenclature. In 1940, the International Union of Pure and Applied Chemistry (IUPAC) recommended that the term 'oxidation number' replace the Stock number.

Sodium and potassium metals react very violently with water and acids, so they are not used in school laboratories. Both of these metals are stored under kerosene. They oxidise readily in water; hence, they are more reactive than calcium. Potassium is more reactive than sodium and its reactions are more violent. Potassium metal is banned in many educational jurisdictions across Australia, while sodium metal can be used only in teacher demonstrations.

We can use the results of Experiment 3.1 and the information about sodium and potassium to expand the activity series further:

$$K > Na > Ca > Mg > Zn > Fe > Cu > Ag$$

ALKALI METALS IN WATER, ACCURATE!

Watch this video, which shows some chemical and physical properties of alkali metals – hardness, reactivity in air and reactivity in water.

Halogen displacement reactions

Halogen displacement reactions are also examples of redox reactions. A halogen displacement reaction occurs when a halogen is added to an ionic solution containing the ion of another halogen (a halide solution). The cation in this solution is a spectator ion, as it does not take part in the chemical reaction.

The general equation for a halogen displacement reaction is written as:

$$\underset{\text{Halide}_1}{2AB(aq)} + \underset{\text{Halogen}_2}{C_2(aq)} \rightarrow \underset{\text{Halide}_2}{2AC(aq)} + \underset{\text{Halogen}_1}{B_2(aq)}$$

EXPERIMENT 3.2

HALOGEN DISPLACEMENT REACTIONS

You will use combinations of halogens and solutions of these halides to rank the halogens from most reactive to least reactive; that is, those most likely to be reduced to least likely to be reduced.

Aim

To rank the halogens from most likely to be reduced to least likely to be reduced

Materials

- 50 mL dropper bottles of:
  - 0.1 mol L^{-1} potassium chloride
  - 0.1 mol L^{-1} potassium bromide
  - 0.1 mol L^{-1} potassium iodide
  - bromine water
  - iodine water

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Bromine water and iodine water produce irritating vapours.	Use small quantities in a well-ventilated area such as a fume hood.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1 Pour about 1 cm depth of each of the halides into separate test tubes.

2 Add about 4 drops of bromine water to each test tube.

3 Record your observations.
4 Repeat the experiment using iodine water instead of bromine water.

Results

1 Draw a table in which the halogens are across the top and the halide solutions are down the side.
2 Record your results in the table, using either words or photos. Remember – no reaction is also a result.

Analysis of results

1 Identify the combinations of halogens and halides for which chemical reactions occurred.
2 Which halide was most reactive?
3 Which halide was least reactive?
4 For each of the reactions that occurred:
   a write the overall balanced equation.
   b write the net ionic equation.
   c write the two half-equations.
   d identify the oxidant and the reductant.

Discussion

1 Identify the halogen that was most easily reduced and relate it to its reactivity.
2 Identify the halogen that was least easily reduced and relate it to its reactivity.



DISPLACEMENT REACTIONS IN THE HALOGENS

Complete this simulation, which also includes the use of chlorine water. It can be done in place of Experiment 3.2 by including the Analysis of results and Discussion questions from Experiment 3.2.

QUESTION SET 3.1

Remembering

1 Define:
   a oxidation and reduction.
   b half-equation.
2 Write the mnemonic for redox.

Understanding

3 Explain why oxidation and reduction must always occur as a pair.

Applying

4 Write the oxidation and reduction half-equations for:
   a calcium metal reacting with hydrochloric acid.
   b magnesium metal in an iron(II) solution.
   c copper metal in silver solution.
   d chlorine water in sodium iodide.

Analysing

5 Use the activity series to justify whether a chemical reaction will occur for:
   a zinc metal in a silver solution.
   b zinc metal in a sodium solution.
   c magnesium metal in a copper(II) solution.
   d iron metal in a copper(II) solution.
   e iodine water in calcium chloride.
   f bromine water in zinc iodide.

3.3 Reactivity and the periodic table

The most chemically stable elements on the periodic table are the noble gases (helium to radon). Chemical stability relates to the arrangement of electrons in the atom, in particular, the valence, or outer, shell of electrons. You looked at the arrangement of electrons in atoms in *Nelson Chemistry Units 1 & 2* Chapter 1 and the formation of ions in *Nelson Chemistry Units 1 & 2* Chapter 3. Metals become chemically stable by losing some or all of their valence electrons to form cations. For example, magnesium has a total of 12 electrons. Its electron configuration is 2, 8, 2. Neon is the nearest noble gas to magnesium on the periodic table, with an electron configuration of 2, 8. To become chemically stable, magnesium will lose two electrons so that it achieves the same stable electron configuration as neon. Hence, the magnesium ion has a 2+ charge since it has 10 electrons but 12 protons. The formula for the magnesium ion is Mg^{2+}.

Non-metals become chemically stable by gaining electrons to form anions. For example, chlorine has a total of 17 electrons. Its electron configuration is 2, 8, 7. Argon is the nearest noble gas to chlorine on the periodic table, with an electron configuration of 2, 8, 8. To become chemically stable, chlorine gains one electron so that it achieves the same stable electron configuration as argon. Hence, the chloride ion has a 1− charge since it has 18 electrons but 17 protons. The formula for the chloride ion is Cl^-.

These general rules explain why metals tend to be oxidised to form cations while non-metals tend to be reduced to form anions. However, it does not explain why some metals are more reactive than others and can displace them from solution.

ACTIVITY 3.1

PERIODIC TABLE AND REACTIVITY

Aim

To identify simple trends between position on periodic table and reactivity

You will need

- Blank periodic table as shown in Figure C3.4
- Results of Experiment 3.1

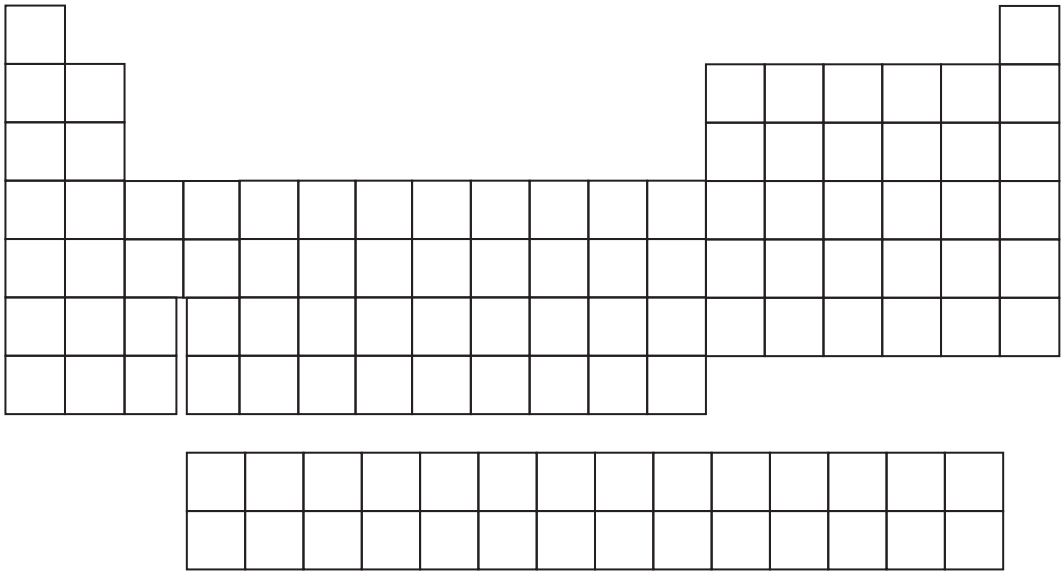


Figure C3.4 Blank periodic table

What to do

Place the following elements on your blank periodic table.

a All noble gases

b Fluorine, chlorine and bromine

c All elements in the activity series on page 210

What did you discover?

1 Compare the reactivity of the metals in groups 1 and 2 as you move down the group.

2 Compare the reactivity of the transition metals in period 4 with the period 4 metals in groups 1 and 2.

Since chemical reactions involve the rearrangement of electrons so that each chemical species present achieves an electron configuration similar to its nearest noble gas, there must be a link between the ability of a chemical species to attract electrons and its reactivity. In *Nelson Chemistry Units 1 & 2* Chapter 1, you revised the model of an atom, which indicated that:

- there is a positively charged nucleus containing protons and neutrons
- electrons are arranged in distinct shells, or energy levels, around the nucleus
- the innermost shell can only contain two electrons since there is a balance between the force of attraction between the nucleus and the electrons and the force of repulsion between the electrons
- the number of electrons in a shell increases as the distance of the shell from the nucleus increases. It is the valence electrons that are involved in chemical reactions.

Three factors that need to be considered are the:

- number of protons in the nucleus – the greater the number of protons, the greater the force of attraction between the nucleus and the valence electrons.
- distance of the valence electrons from the nucleus – the greater the distance of the valence electrons from the nucleus, the smaller the force of attraction between the nucleus and the valence electrons
- number of shells between the valence shell and the nucleus that are shielding the valence electrons from the nucleus – the greater the number of shells of electrons between the valence electrons and the nucleus, the smaller the force of attraction between the nucleus and the valence electrons.

Ionisation energy

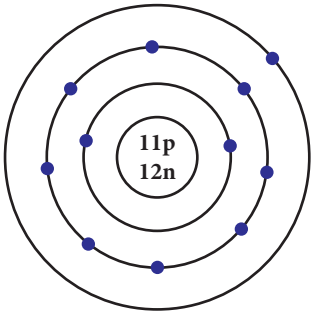
Ionisation energy is the energy required to remove one electron from a gaseous species. The first ionisation energy is the energy required to remove one electron from a gaseous atom to form a gaseous ion. It can be written as:

$$E(g) \rightarrow E^{+}(g) + e^{-}$$

The second ionisation energy is the energy needed to remove one more electron from the ion:

$$E^{+}(g) \rightarrow E^{2+}(g) + e^{-}$$

Ionisation energy is the energy required to remove one electron from a gaseous species.



◀ **Figure C3.5**
Sodium atom. Ionisation removes the electron in the outer shell.

An element has as many ionisation energies as it has electrons. Sodium has 11 electrons, so it has 11 ionisation energies. Chlorine has 17 electrons, so it has 17 ionisation energies.

As more electrons are removed, the ratio of protons to electrons changes and hence a greater force of attraction occurs between the nucleus and the remaining electrons. Therefore, the energy to remove each successive electron increases. As more electrons are removed, electrons from shells closer to the nucleus are removed, which requires more energy to overcome the force of attraction between the nucleus and the valence electrons. Table C3.1 shows the first four ionisation energies for sodium, magnesium and aluminium.



To see how this knowledge of reactivity is applied, refer to Context 3, 'Alternative sources of energy', page 64.

Table C3.1 Ionisation energies required to remove the first four electrons

Ionisation energy ($kJ\,mol^{-1}$)	Sodium	Magnesium	Aluminium
1st	486	738	576
2nd	4562	1451	1817
3rd	6910	7733	2745
4th	9543	10543	11577

ACTIVITY 3.2

IONISATION ENERGY AND VALENCY

Aim

To identify the relationship between ionisation energy and valency

What to do

1 Draw a diagram to show the structure of each of the following. Clearly indicate the number of protons in the nucleus and the arrangement of electrons in each shell.
   - **a** Sodium atom
   - **b** Sodium ion with one electron removed
   - **c** Sodium ion with two electrons removed
   - **d** Sodium ion with three electrons removed

2 Draw a diagram to show the structure of each of the following. Clearly indicate the number of protons in the nucleus and the arrangement of electrons in each shell.
   - **a** Magnesium atom
   - **b** Magnesium ion with one electron removed
   - **c** Magnesium ion with two electrons removed
   - **d** Magnesium ion with three electrons removed

3 Draw a diagram to show the structure of each of the following. Clearly indicate the number of protons in the nucleus and the arrangement of electrons in each shell.
   - **a** Aluminium atom
   - **b** Aluminium ion with one electron removed
   - **c** Aluminium ion with two electrons removed
   - **d** Aluminium ion with three electrons removed

4 Refer to Table C3.1 to explain why:
   - **a** sodium has the lowest first ionisation energy.
   - **b** sodium has such a large second ionisation energy.
   - **c** there is such a large increase between the second and third ionisation energies for magnesium.

d aluminium has the lowest third ionisation energy.

e there is such a large increase between the third and fourth ionisation energies for aluminium.

What did you discover?

Refer to Table C3.1 and the structure of the atom to justify why:

a sodium has a 1+ valency.

b magnesium has a 2+ valency.

c aluminium has a 3+ valency.

WEBELEMENTS

Visit this website for comprehensive information on the properties of each of the elements, including ionisation energies.

ACTIVITY 3.3

TRENDS IN IONISATION ENERGIES

Aim

To describe the trends in ionisation energies both across a period and down a group

You will need

- Graph paper or spreadsheet program such as Microsoft Excel or Apple Numbers
- First ionisation energies for elements in period 3 (Na to Ar)
- First ionisation energies for elements in group 1 (Li to Cs)
- First ionisation energies for elements in group 17 (F to At)

What to do

1 Graph the data of first ionisation energy versus atomic number for the elements in period 3.

2 Graph the data of first ionisation energy versus atomic number for the elements in group 1.

3 Graph the data of first ionisation energy versus atomic number for the elements in group 17.

4 Compare the first ionisation energies for elements in groups 1 and 17 in the corresponding period of the periodic table.

5 Identify which of the following factors has the greatest impact on the difference in the ionisation energy as you move from left to right across a period – number of protons, distance of valence electrons from the nucleus, number of shells between the valence shell and the nucleus.

6 Identify which of the following factors has the greatest impact on the difference in the ionisation energy as you move down a group – number of protons, distance of valence electrons from the nucleus, number of shells between the valence shell and the nucleus.

What did you discover?

1 Use your period 3 graph to describe the general trend for ionisation energies across a period.

2 Use your data for groups 1 and 17 to describe the general trend for ionisation energies down a group.

3 Justify the trend for first ionisation energy across a period.

4 Justify the trend for first ionisation energy down a group.

5 Explain the trend for first ionisation energies for the groups 1 and 17 elements in the corresponding period of the periodic table.

QUESTION SET 3.2

Remembering

1 Identify three factors that must be considered when assessing the stability of an atom.
2 Define 'ionisation energy'.

Understanding

3 Write the electron configuration for an:
   a oxygen atom.
   b oxide ion.
4 Explain why:
   a strontium forms a 2+ ion.
   b aluminium forms a 3+ ion.
5 How many ionisation energies would bromine have? Justify your answer.

Applying

6 Justify the formula for the phosphide ion.
7 Justify why fluorine has a larger first ionisation energy than bromine.

Analysing

8 Justify whether there is a large increase in ionisation energy between the first and second ionisation energies for calcium.
9 Justify whether sulfur or magnesium would have a larger first ionisation energy.

Reflecting

10 How does an understanding of ionisation energy help to explain the reactivity of metals?

3.4 Returning to reactivity

The positions of the elements on the periodic table and the trends in ionisation energy explain much about the activity series of metals. It explains why calcium is more reactive than magnesium. It explains why calcium is more reactive than iron. It explains why iron is more reactive than copper. However, it does not explain why zinc is more reactive than copper.

Figure C3.6 ▶
Activity series of metals

K > Na > Li > Ba > Ca > Mg > Al > Zn > Fe > Sn > Pb > (H) > Cu > Ag > Pt > Au

So far, we've looked at trend data. However, there are slight differences when individual data points are analysed. Both zinc and copper form 2+ ions. Zinc's second ionisation energy is lower than copper's. Hence, Zn^{2+} forms more readily than Cu^{2+}. Many factors must be considered to determine the reactivity of an element. It is important that we don't oversimplify the chemistry.

Corrosion

In its simplest form, **corrosion** is the oxidation of a metal in the presence of air to form the metal oxide. The reaction is actually between the metal and the oxygen in the air. The water vapour also present in air acts as the **electrolyte** for the transfer of the electrons from the metal to the oxygen.

$$\text{Metal} + \text{oxygen} \rightarrow \text{metal oxide}$$

This is a spontaneous chemical reaction. However, it is also a very slow reaction. Corrosion takes time. For example, magnesium reacts with oxygen to form magnesium oxide.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

A strip of magnesium metal that is exposed to the air for a period of time will lose some of its lustre. This is because it has oxidised to form magnesium oxide. This happens to many metals. This is why you use sandpaper to clean the metals before use in experiments – to remove the outer oxide layer so that it is the metal that is taking part in the reaction.

The most common example of corrosion is rust. **Rust** is hydrated iron(III) oxide, which is produced when iron corrodes. Overall, the simplified reaction is:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

The chemistry is a little more complicated than this simplified reaction suggests. The half-equations for this reaction are:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$
$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

Overall, this reaction becomes:

$$2Fe\ (s) + O_2(g) + 2H_2O(l) \rightarrow 4OH^-(aq) + 2Fe^{2+}(aq)$$

The products of this reaction form an iron(II) hydroxide precipitate, $Fe(OH)_2$, which further oxidises to form the hydrated iron(III) oxide, which we call rust.

$$4Fe(OH)_2(s) + O_2(g) \rightarrow 2(Fe_2O_3.H_2O)(s) + 2H_2O(l)$$

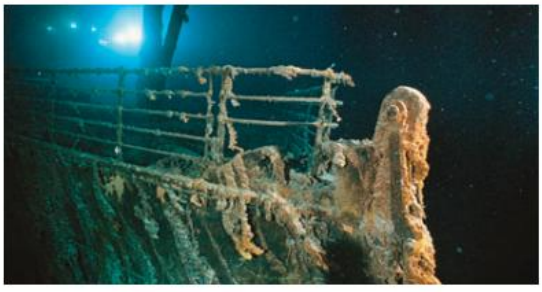
Aluminium is another commonly available metal. It is used for window frames and screen doors. It is also used in aircraft because it is strong but much lighter than steel. It oxidises to form aluminium oxide, Al_2O_3. Aluminium does not appear to corrode as much as iron. The reason for this is that aluminium is a **passivating** metal. It reacts to form aluminium oxide but this oxide binds tightly to the surface of the metal to form an **impervious** layer to oxygen and water, which prevents the metal underneath from corroding further.

However, iron does not form an impervious oxide layer. Rust is a red-brown colour and it flakes off the surface of the metal, allowing the surface of the metal to continue to react with oxygen and form more rust.

WOW

Corrosion of the *Titanic*

Scientists had to re-think their definition of corrosion when they finally saw the hull of the RMS *Titanic* for the first time after it had been submerged for more than 73 years at the bottom of the Atlantic Ocean. They expected only a small amount of corrosion since there was very little oxygen at great depths and the rate of reaction was expected to be very slow at such low temperatures. However, there was significant corrosion. Upon further investigation, the scientists realised that bacteria had produced acidic micro-environments, which promoted corrosion. Other bacteria present respired by the reduction of sulfate. Therefore, iron oxidised since there was a reduction reaction. This accounted for the significant corrosion of the RMS *Titanic*.



Emory Kristof/National Geographic Creative

▲ **Figure C3.7** RMS *Titanic*

QUESTION SET 3.3

Remembering

1 Define:
- a corrosion.
- b passivating.

Understanding

2 Aluminium is a more reactive metal than iron. Explain why iron oxidises readily to form rust while aluminium does not corrode as easily.

Applying

3 Which element in each of the following pairs is more likely to be reduced?
- a Magnesium or lead
- b Copper or chlorine
- c Barium or hydrogen

4 Write a balanced equation for the corrosion of zinc.

3.5 Oxidation states

In the simple examples used so far, it is easy to determine which species is being oxidised and which is being reduced. However, sometimes it is difficult to determine whether an oxidation–reduction reaction is occurring or not. To assist with this, scientists have developed **oxidation states**, sometimes referred to as oxidation numbers.

Oxidation state is an indication of the number of electrons an atom would gain or lose to get to its present state. It assumes that each species is completely ionic.

The oxidation state always indicates whether it has a positive or negative charge. It is straightforward to determine the oxidation states of simple ionic compounds such as sodium sulfide, Na_2S. The sodium ion is written as Na^+. It has a +1 oxidation state. The sulfide ion is written as S^{2-}. It has a –2 oxidation state.

WOW

Oxidation state

The definition for oxidation state has been modified several times since the German chemist Wendell Mitchell Latimer first defined it in 1938. IUPAC indicates that oxidation state and oxidation number are defined differently. However, they are commonly used interchangeably.

For an example of different oxidation states of vanadium and its use in a battery, refer to Context 3, 'Alternative sources of energy', page 72.

For an example of the use of oxidation states of chromium in breathalysers, refer to Context 1, 'Wine', page 25.

However, in covalent molecules, electrons are shared by different species. It is more difficult to determine the oxidation states, and hence to determine if a redox reaction has occurred or not.

The following rules can be used when determining the oxidation states of various species:

1. The oxidation state of any element is zero.
2. The oxidation state of a monatomic ion is the same as the charge on that ion.
3. The oxidation state of hydrogen in compounds is always +1, except when forming metal hydrides when it is –1.
4. The oxidation state of oxygen in any compound is always –2, except when forming peroxides where it is –1 and in F_2O where it is +2.
5. In a neutral compound, the sum of the oxidation states must always equal zero.
6. In ions, the sum of the oxidation states must always equal the charge on the ion.
7. The most electronegative species in a compound is assigned the negative oxidation state; the less electronegative species is assigned the positive oxidation state.

WORKED EXAMPLE 3.2

a Determine the oxidation state of the various species in methane, CH_4.

b Determine the oxidation state of the various species in the phosphate ion, PO_4^{3-}.

Answers

a Oxidation state of hydrogen = +1

Oxidation state of carbon = −4

Logic

1 Rule 3 says that hydrogen has an oxidation state of +1. Therefore, since there are 4 hydrogens, there is a total oxidation state of +4 due to the hydrogens.

2 Rule 5 says that the sum of the oxidation states on the neutral compound must equal zero. Therefore, the oxidation state of carbon must be −4.

b Oxidation state of oxygen = −2

Oxidation state of phosphorus = +5

1 Rule 4 says that oxygen has an oxidation state of −2. Since there are 4 oxygens, the total oxidation state is −8 due to the oxygens.

2 Rule 6 says that in ions, the sum of the oxidation states must equal the charge on the ion. Hence, the sum of the oxidation states for the phosphate ion, PO_4^{3-}, must equal −3. Therefore, the oxidation state of the phosphorus must be +5.

Try these yourself

a Determine the oxidation state of chromium in the dichromate ion, $Cr_2O_7^{2-}$.

b Determine the oxidation state of nitrogen in dinitrogen tetraoxide, N_2O_4.

Using oxidation states to write half-equations

Oxidation states can be used to write half-equations for ions. The simplest form has been used in previous sections where electrons were used to balance the charge in the half-equation. The two species were written and electrons were added to the side that was more positive to balance the charge.

WORKED EXAMPLE 3.3

a Magnesium has an oxidation state of zero since it is an element. The magnesium ion has an oxidation state of +2. Write an equation to show this reaction.

b Chlorine gas undergoes a reduction reaction to form chloride ions. Write a balanced equation for this half-reaction.

Answers

a $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

Logic

1 $Mg(s) \rightarrow Mg^{2+}(aq)$

There is one magnesium on each side of the equation. However, the charge is not balanced. The charge on the left-hand side is zero, while the charge on the right-hand side is +2.

2 To balance the charge, add 2 electrons to the right-hand side.

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

The charge on the right-hand side is now zero.

Therefore, the charge on the left-hand side equals the charge on the right-hand side.

b $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

1 $Cl_2(g) \rightarrow 2Cl^-(aq)$

There are two chlorines on each side of the equation. However, the charge on the left-hand side is zero, since chlorine is an element. The total charge on the right-hand side is −2 since there are 2 chlorides, each with a charge of −1.

2 To balance the charge, add 2 electrons to the left-hand side.

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

The total charge on the left-hand side is now −2.

Therefore, the charge on the left-hand side equals the charge on the right-hand side.

Try these yourself

a Aluminium oxidises to form the aluminium ion. Write a balanced equation for this half-reaction.

b Bromine is reduced to form the bromide ion. Write a balanced equation for this half-reaction.

c Iron(II) oxidises to form iron(III). Write a balanced equation for this half-reaction.

Oxidation states can also be used to write half-equations for more complex ions, such as the permanganate ion and the chromate ion. The method is a little more complex; the following rules can be used.

1 Use trial and error to balance all elements except hydrogen and oxygen.
2 Balance oxygen by adding water to the side that is deficient in oxygen.
3 Balance hydrogen by adding H^+ in acidic solutions to the side deficient in hydrogen.
4 Balance the charge by adding electrons to the side that has an excess of positive charge.

WORKED EXAMPLE 3.4

Write balanced half-equations for the reduction of:

a permanganate, MnO_4^-, in acidic solution.

b dichromate ion, $Cr_2O_7^{2-}$, in acidic solution.

Answers

a $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

b $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Logic

a

1 Manganese in the permanganate ion, MnO_4^-, has an oxidation state of +7. Manganese can also exist as a +2 ion. This reaction occurs in an acidic solution.

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$

There is one manganese on each side of the equation.

2 Balance the oxygens. Add 4 moles of water to the right-hand side since each water contains 1 oxygen, and 4 oxygens are needed to balance the oxygens on the left-hand side.

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

3 Balance the hydrogens. Since this reaction occurs in an acidic solution, add 8 hydrogen ions (H^+) to the left-hand side to balance the hydrogens on the right-hand side.

$MnO_4^-(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

4 Balance the charge. Charge on left-hand side is +7 while the charge on the right-hand side is +2. Add 5 electrons to the left-hand side.

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

b

1 Chromium in the dichromate ion, $Cr_2O_7^{2-}$, has an oxidation state of +6. Chromium can also exist as a +3 ion. This reaction occurs in an acidic solution.

$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$

There are two chromiums on each side of the equation.

2 Balance the oxygens. Add 7 moles of water to the right-hand side since each water contains 1 oxygen and 7 oxygens are needed to balance the oxygens on the left-hand side.

$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

3 Balance the hydrogens. Since this reaction occurs in an acidic solution, 14 hydrogen ions (H^+) are added to the left side since it is deficient in hydrogens.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

4 Balance the charge. Charge on left-hand side is +12 while the charge on the right-hand side is +6. Add 6 electrons to the left-hand side.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Try these yourself

Write balanced half-equations for:

a sulfur dioxide oxidising in acidic solution to form the sulfate ion.

b the chlorate ion, ClO_3^-, being reduced in acidic solutions to form chlorine dioxide, ClO_2.

3.6 Combustion is a redox reaction

It is easy to identify metal displacement reactions and corrosion reactions as oxidation–reduction reactions because it is easy to see that one of the species in these reactions is oxidised and the other is reduced. Combustion does not 'look' like a redox reaction, but if you analyse the oxidation states of the species in the equation, then you will see that one of the species is oxidised and another is reduced.

Oxidation occurs when the oxidation state increases, becomes more positive.
Reduction occurs when the oxidation state decreases, becomes more negative.

Consider the combustion of methane:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

- In methane, CH_4, hydrogen has an oxidation state of +1 (rule 3), so carbon must have an oxidation state of −4.
- In oxygen, O_2, oxygen has an oxidation state of zero (rule 1).
- In carbon dioxide, CO_2, oxygen has an oxidation state of −2 (rule 4), so carbon must have an oxidation state of +4.
- In water, H_2O, oxygen has an oxidation state of −2 (rule 4) and hydrogen has an oxidation state of +1 (rule 3).

Therefore, during the reaction, the oxidation state of oxygen changes from 0 to −2 and the oxidation state of carbon changes from −4 to +4. Hence, oxygen is reduced, since its oxidation state becomes more negative, and carbon is oxidised, since its oxidation state becomes more positive. This is an oxidation–reduction reaction.



D. Pimborough/Shutterstock.com

◀ **Figure C3.8**
A gas hot plate burning natural gas is an example of a redox reaction.

QUESTION SET 3.4

Remembering

1 Define 'oxidation state'.

2 What is the oxidation state of an element?

3 The oxidation state of oxygen in any compound is always −2. What are the exceptions to this rule?

Understanding

4 Use the combustion of ethylene to explain why a combustion reaction is an example of a redox reaction.

Applying

5 Identify the oxidation state of the underlined species.

a $\underline{I}O_3^-$

b $\underline{Cr}O_4^{2-}$

c $\underline{C}_2H_2$

d $H_3\underline{As}O_4$

e $\underline{Cl}O_3^-$

Analysing

6 Write a balanced half-equation for the reduction of Bi^{3+} to form BiO_3^- in an acidic solution.

CHAPTER CHECKLIST

You should know:

- displacement reactions of metals, combustion and corrosion are examples of redox reactions
- oxidation involves the loss of electrons
- reduction involves the gain of electrons
- more reactive metals will displace less reactive metals from solution
- factors that affect the reactivity of atoms include the:
  - number of protons in the nucleus
  - distance of the valence electrons from the nucleus
  - number of shells between the valence shell and the nucleus that are shielding the valence electrons from the nucleus
- ionisation energy is the energy required to remove one electron from a gaseous species
- reactivity of elements is related to their ionisation energy
- the rules for determining oxidation states.

You should be able to:

- write net ionic equations for metal displacement reactions
- write oxidation and reduction half-equations
- write electron configurations for common elements and ions
- write equations to show first and subsequent ionisation energies
- determine the valency of a simple ion from a table of successive ionisation energies
- determine the oxidation state of a given species in ionic compounds, polyatomic ions and covalent molecules
- use oxidation states to write balanced half-equations for oxidation or reduction reactions.

CHAPTER GLOSSARY

corrosion the oxidation of a metal in the presence of oxygen to form the metal oxide

electrolyte a substance that conducts an electric current

half-equation when an equation has been split into its two components – the oxidation reaction or the reduction reaction

impervious does not allow particular substances to pass through

ionisation energy the energy required to remove one electron from an atom or ion of an element in a gaseous state

oxidant or oxidising agent a chemical species that causes another species to be oxidised

oxidation loss of electrons

oxidation state the number of electrons that an atom would have gained or lost to get to its present state; it assumes that each species is completely ionic

passivating a metal that forms an impervious oxide layer on its surface, which prevents further corrosion

redox reaction a reaction that involves the oxidation of one species and the reduction of another species

reductant or reducing agent a chemical species that causes another species to be reduced

reduction gain of electrons

rust hydrated iron(III) oxide ($Fe_2O_3.xH_2O$)

CHAPTER REVIEW QUESTIONS

Remembering

1 Identify whether the following statements are true or false. Correct any false statements and rewrite them to make them true.
   - a Oxidation occurs when a species gains electrons.
   - b A metal reacting with an acid is an example of a redox reaction.
   - c Magnesium is more reactive than copper and reduces preferentially in the presence of copper.
   - d A reducing agent gains electrons.
   - e The first ionisation energy is the energy required to remove one electron from an element in its gaseous state.
   - f A passivating metal forms an impervious oxide layer when it reacts with oxygen to prevent further oxidation of the metal.

Understanding

2 Explain why oxidation reactions can only occur when a reduction reaction occurs simultaneously on another species.

3 Explain why sodium is less reactive than potassium.

4 Explain why fluorine is the most reactive non-metal on the periodic table.

5 Explain why calcium's third ionisation energy is much greater than its second.

6 Justify why chlorine is more likely to be reduced than magnesium.

Applying

7 Identify whether the underlined species is undergoing oxidation or reduction.
   - a $Zn(s) + 2\underline{Fe}^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$
   - b $\underline{Cu}(s) + 2NO_3^-(aq) + 4H_3O^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 6H_2O(l)$
   - c $4\underline{Mn}O_4^-(aq) + 12H_3O^+(Aq) \rightarrow 4Mn^{2+}(aq) + 5O_2(g) + 18H_2O(l)$
   - d $Mg(s) + \underline{Cl}_2(g) \rightarrow MgCl_2(aq)$
   - e $Fe_2O_3(s) + 2\underline{Al}(s) \rightarrow Al_2O_3(s) + 2Fe(l)$
   - f $2\underline{H}_2O(l) \rightarrow 2H_2(g) + O_2(g)$

8 Determine the oxidation state of the underlined species.
   - a $\underline{S}O_4^{2-}(aq)$
   - b $H\underline{Cl}(aq)$
   - c $\underline{N}H_4^+(aq)$
   - d $\underline{V}O^{2+}(aq)$
   - e $Li\underline{Co}O_2(aq)$

Analysing

9 Determine whether the following reactions are oxidation–reduction reactions. For any redox reaction, identify the species being oxidised and the species being reduced.

a $2Al(s) + 3FeCl_2(aq) \rightarrow 2AlCl_3(aq) + 3Fe(s)$

b $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

c $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

d $2Ni(OH)_3(aq) + Cd(s) \rightarrow 2Ni(OH)_2(aq) + Cd(OH)_2(aq)$

e $Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow 2KNO_3(Aq) + PbI_2(s)$

10 The following table contains the first ionisation energy of five consecutive elements. Use the table to answer the questions below.

Element	Ionisation energy ($kJ\,mol^{-1}$)
R	1006
S	1257
T	1527
U	425
V	596

a Identify an element that would form an ionic compound with Br^-.

b Which element would be in the same group as oxygen?

c Which element is an inert gas?

11 Use oxidation states to write balanced half-equations for the following reactions in an acidic solution.

a In the vanadium redox cell, one of the half-equations involves converting VO_2^+ to VO^{2+}.

b Nitrous acid, HNO_2, changes to the nitrate ion, NO_3^-.

c Ethanol oxidises to form acetic acid, CH_3COOH.

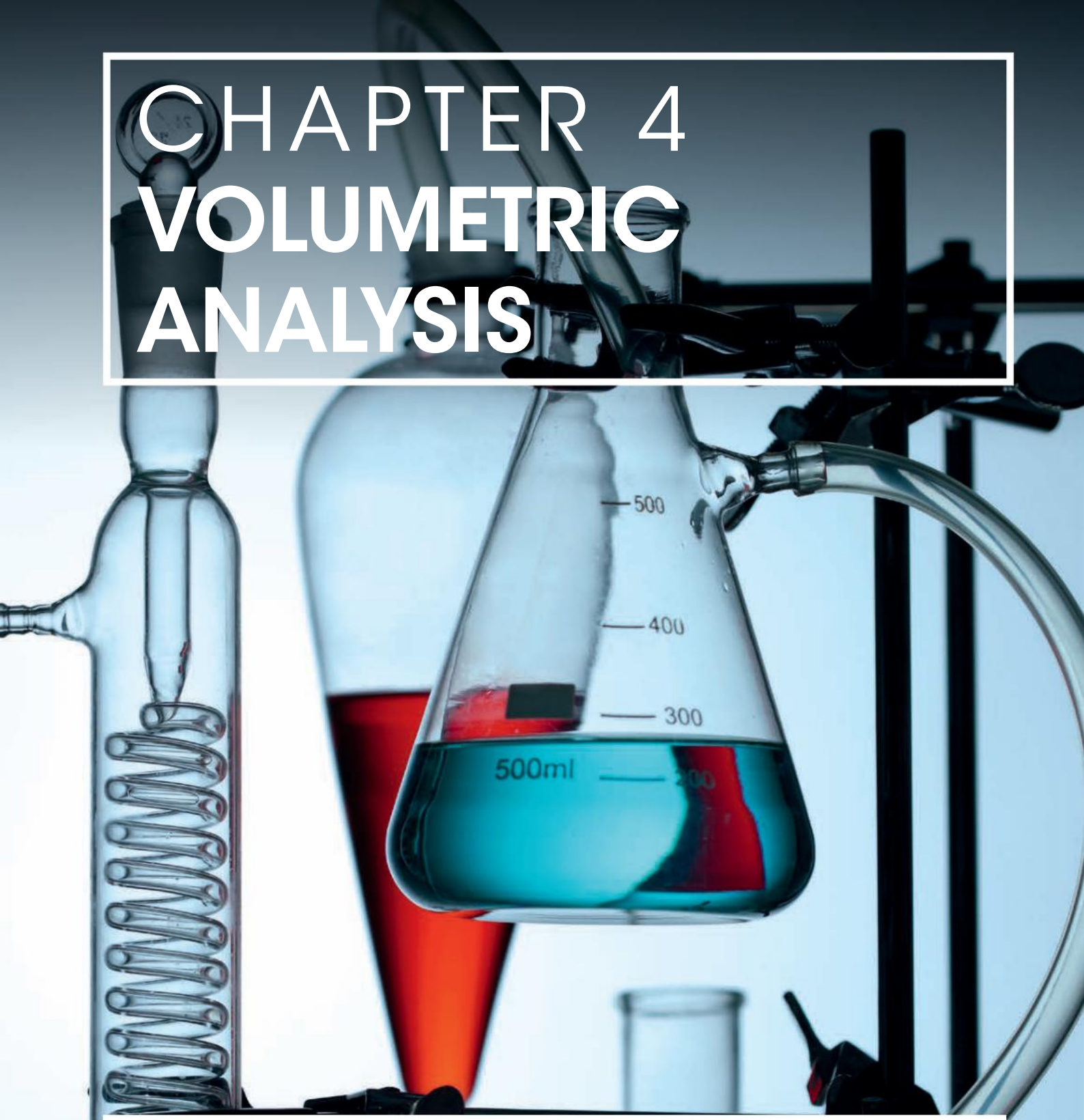
Evaluating

12 Decomposition reactions and synthesis reactions are both examples of redox reactions. Assess this statement with reference to specific examples.

Reflecting

13 Discuss whether understanding redox chemistry assists with understanding the chemistry of both corrosion and combustion.

CHAPTER 4
VOLUMETRIC ANALYSIS



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By the end of this chapter you will have covered the following material.

Science Understanding

- Acid–base indicators are weak acids or bases where the acidic form is of a different colour to the basic form (ACSCH101)
- Volumetric analysis methods involving acid–base reactions rely on the identification of an equivalence point by measuring the associated change in pH, using chemical indicators or pH meters, to reveal an observable end point (ACSCH102)

4.1 Introduction

Determining whether or not a chemical reaction has occurred is a form of qualitative analysis – it gives a 'yes/no' answer. However, there are times when chemists want not only to know whether a chemical reaction occurs, but they also want to be able to quantify the reaction. For this, they need to be able to perform quantitative analyses. **Volumetric analysis** is one type of quantitative analysis. Volumetric means measuring volumes. Hence, volumetric analysis involves determining the concentration of a sample by measuring the volume of this sample that reacts with a known volume of another substance of known concentration.

Volumetric analysis involves determining the concentration of a sample by measuring the volume of this sample that reacts with a known volume of another substance of known concentration.

4.2 Volumetric analysis – the basics

Titration is the main technique for volumetric analysis. This involves determining the **equivalence point**. Consider the following reaction:

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

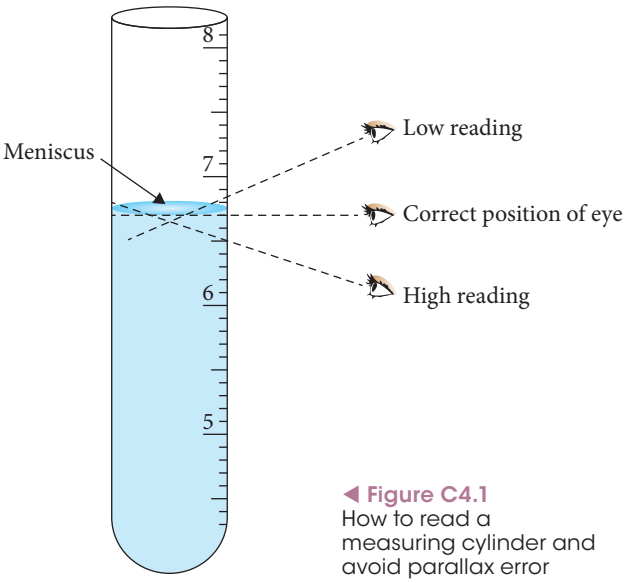
The mole ratio indicates that 2 moles of sodium hydroxide react with 1 mole of sulfuric acid. The equivalence point is the point at which there are twice as many moles of sodium hydroxide present as there are moles of sulfuric acid. This is because 1 mole of sulfuric acid produces 2 moles of hydrogen ions (H^+) and 2 moles of sodium hydroxide produce 2 moles of hydroxide ions (OH^-). Therefore, there are an equal number of moles of hydrogen ions and hydroxide ions. Hence, the equivalence point is the point at which the reactants are present in the mole ratio given in the balanced equation for this reaction.

In the reaction above, both solutions are clear, as are the products. It is not possible to see when the equivalence point has been reached. Acid–base indicators change colour within certain pH ranges. An acid–base indicator is added to indicate when the **endpoint** has been reached. The endpoint is indicated by a change in colour.

Titrations use some specialist glassware and the endpoint can be detected by a variety of methods, such as the use of acid–base indicators, conductivity and pH probes. Chemists must have an understanding of the chemistry of the specific reaction to determine the most appropriate way to determine the endpoint.

METHODOLOGY FOR USING SPECIALISED GLASSWARE

Visit this website for descriptions, diagrams and step-by-step videos of using glassware such as burettes, volumetric flasks and volumetric pipettes.



◀ Figure C4.1
How to read a measuring cylinder and avoid parallax error

Specialised glassware

Volumetric analysis involves the measuring of volumes, so you need to use glassware with accurate measuring scales. The most common types of glassware are volumetric flasks, burettes and pipettes. Since **accuracy** is very important in this technique, you must minimise **parallax error** by ensuring that when reading the volume, the measuring line is directly in line with your eye level.

Volumetric flask

A volumetric flask is a flat-bottomed flask with a long narrow neck. You used these in Year 11 for accurately diluting a solution. Volumetric flasks are available in a variety of sizes but the most commonly used flasks in schools are the 100 mL and 250 mL volumetric flasks. A line on the flask indicates the volume that can be accurately measured. The volumetric flask is always rinsed with the solvent, generally water, prior to use.

Once the flask has been rinsed with the solvent, pour the solution into the flask and top it up to the line with a wash bottle or a Pasteur pipette – a dispenser with a fine tip to add small drops. The bottom of the meniscus must be just touching the line on the flask. It is important not to overfill the flask, because then the volume of solution will not be accurately known. If this happens, you will need to empty the flask and start again from the beginning.



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▲ **Figure C4.2**
Volumetric flask

Burette

A burette is a long, narrow glass tube with a tap at the bottom. The most commonly used burette is a 50 mL burette. The measuring scale on a burette is inverted, since it measures the volume of solution that leaves the burette through the tap. Hence, the zero position is at the top of the burette and the 50 mL position is near the bottom of the burette. The burette is always rinsed with the solution that will be placed in the burette prior to use.

To rinse the burette, pour a small volume of solution into the burette. Then, holding the burette horizontally, open the tap and turn the burette slowly in your hands so that all surfaces on the inside of the burette are rinsed with the solution. Empty this solution.

To fill the burette, place it back in the burette clamp and close the tap. Pour the solution into the burette until it is above the zero mark. Place a flask under the burette and open the tap so that the airlock below the tap is filled with solution. Adjust the volume of solution in the burette to the zero mark.

Pipette

A pipette is a thin glass tube that accurately measures a fixed volume of solution. The most common pipettes in school laboratories are 20 mL and 25 mL pipettes. A line on the pipette indicates the volume that can be accurately measured. The pipette is always rinsed with the solution that will be placed in it prior to use.

To rinse the pipette, use a pipette filler to draw up a small volume of solution. Remove the pipette filler, hold the pipette horizontally and turn the pipette in your hands so that all surfaces on the inside of the pipette are rinsed with the solution. Empty this solution.

To fill the pipette, use the pipette filler to draw the solution into the pipette. Stop when the volume of solution is above the line on the pipette. Slowly evacuate the solution until the bottom of the meniscus is just touching the line. Place the pipette over the flask into which the solution will be evacuated, remove the pipette filler and allow the pipette to empty. Tap the tip of the pipette on the inside of the flask. A small volume of solution will remain in the pipette – do not try to evacuate this solution. The pipette has been calibrated to evacuate the specified volume when it empties naturally under gravity.



sciencephotos/Alamy

▲ **Figure C4.4** Pipette



i4lcool2/Shutterstock.com

▲ **Figure C4.3**
Burette

EXPERIMENT 4.1

PRACTISING RINSING AND READING MEASUREMENTS ON GLASSWARE

Volumetric flasks, burettes and pipettes are used to measure accurate volumes. Hence, you need to learn to use this equipment correctly and to read the scales correctly to benefit from using this equipment.

Aim

To use and read volumes accurately using volumetric flasks, burettes and pipettes

Materials

- 100 mL or 250 mL volumetric flask with lid
- 20 mL or 25 mL pipette
- Pipette filler
- Burette
- Burette clamp or bosshead and retort clamp
- Retort stand
- 250 mL conical flask
- Wash bottle or Pasteur pipette and bulb
- Filter funnel
- 250 mL beaker
- 150 mL beaker

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Glassware may break and cut you.	Always ensure that glassware is kept away from the edge of benches. If glassware does break, inform your teacher immediately.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

Part A Volumetric flask

1. Rinse the volumetric flask with a small volume of water, then empty it.
2. Place a filter funnel in the neck of the volumetric flask.
3. Use a 250 mL beaker to pour water through the filter funnel into the flask. Hold the filter funnel slightly above the flask so that the water will flow freely.
4. When the bulb of the flask is filled, remove the filter funnel and use a wash bottle or Pasteur pipette to fill the flask so that the bottom of the meniscus is touching the line marked on the flask.
5. Check your result with your teacher.

Part B Burette

6. Clamp the burette to a retort stand using a burette clamp and close the tap on the burette.
7. Pour a small volume of water into the burette.
8. Remove the burette from the burette clamp, hold it horizontally, open the tap and turn the burette so that all surfaces of the burette are rinsed.
9. Empty the water into the sink.
10. Clamp the burette to the retort stand and close the tap on the burette.
11. Use a 150 mL beaker to fill the burette with water above the zero line.
12. Open the tap to allow water to flow to remove the air lock, and then close the tap.
13. Adjust the water level in the burette to the zero mark.
14. Place a flask under the burette and release exactly 26.30 mL from the burette.
15. Check your result by showing your teacher.
16. Refill your burette and adjust the water level in the burette to the zero mark.
17. Place a flask under the burette and release exactly 15.70 mL from the burette.
18. Check your result with your teacher.

Part C Pipette

19 Attach the pipette filler to the pipette and draw up a small volume of water into the pipette.

20 Hold the pipette horizontally, remove the pipette filler and turn the pipette so that all surfaces of the pipette are rinsed.

21 Empty the pipette.

22 Attach the pipette filler to the pipette and draw water into the pipette until the volume is above the line marked on the pipette.

23 Adjust the volume until the bottom of the meniscus touches the line marked on the pipette.

24 Check your result with your teacher.

25 Place the pipette over the 250 mL conical flask and remove the pipette filler so that the pipette empties into the flask. Tap the tip of the pipette on the inside wall of the flask and rinse down the sides of the flask with water.

Results

Record your results in a table, including equipment, volume and comments by your teacher.

Analysis of results

1 Compare your results with those of other students in the class.

2 Comment on the accuracy of your results.

Discussion

1 Discuss any common sources of error in the class results.

2 Describe ways to overcome these sources of error.

Identifying the endpoint – indicators

During volumetric analysis, you need to be able to determine when the equivalence point has been reached. The physical sign that the equivalence point has been reached is the called the 'endpoint'. A simple way of observing the endpoint for an acid–base reaction is the use of an acid–base indicator. Acid–base indicators are used to visually show when a particular pH is passed. Different indicators change colour at different pH ranges. You were introduced to different acid–base indicators in *Nelson Chemistry Units 1 & 2* Chapter 7.

Acid–base indicators contain weak acids where the acid has a different colour from its conjugate base. Some indicators are found in nature while others are synthesised in the laboratory. Litmus is an example of a naturally occurring indicator while methyl orange is manufactured in a laboratory. Universal indicator is a mixture of indicators; therefore, it has a number of colour changes over the pH range of 1–14.

WOW

Natural acid–base indicators

Litmus is extracted from many species of lichen. Although these lichen are found in many parts of the world, nearly all of the litmus used is extracted and packaged in The Netherlands.

Cochineal is another acid–base indicator, but it is not commonly used today. You would need to grind about 70 000 dried female cochineal insects to make less than 0.5 kg of cochineal powder.

Anthocyanin is an acid–base indicator present in red cabbage, poppies and cornflowers.

INVESTIGATION 4.1

ACID–BASE INDICATORS

Different indicators change colour at different pH regions – acidic, neutral and basic. You will test four commonly used indicators in this first-hand investigation – universal indicator, phenolphthalein, methyl orange and bromothymol blue. Other indicators can also be tested, but these indicators are commonly available in school science laboratories.

What is your aim?

What is the purpose of doing this investigation? Re-read the introduction to assist with determining the aim for this investigation.

What will you need?

1. Which indicators will you use?
2. Which solutions will you use to test your indicators?
3. What other equipment will you need to perform this investigation?
4. What quantities of indicators and solutions will you use for this investigation?

What are the risks?

Complete the risk assessment box to show any risks associated with completing this investigation and ways to manage them.

What are the risks in doing this investigation?	How can you manage these risks to stay safe?

How will you carry out your investigation?

Clearly describe the method you will use, including chemicals, quantities and equipment.

What results will you collect?

1. How many columns will you need for your results table?
2. What will be your headings for each column in your results table?
3. What will be the labels for each row in your results table?

How will you analyse your results?

Are there any trends in your data? Why or why not?

What have you found?

1. Justify whether all indicators have the same colour changes.
2. Justify whether the indicators have the same colour in the same pH regions.
3. Justify whether all indicators have different colours in each pH region.

What do you conclude?

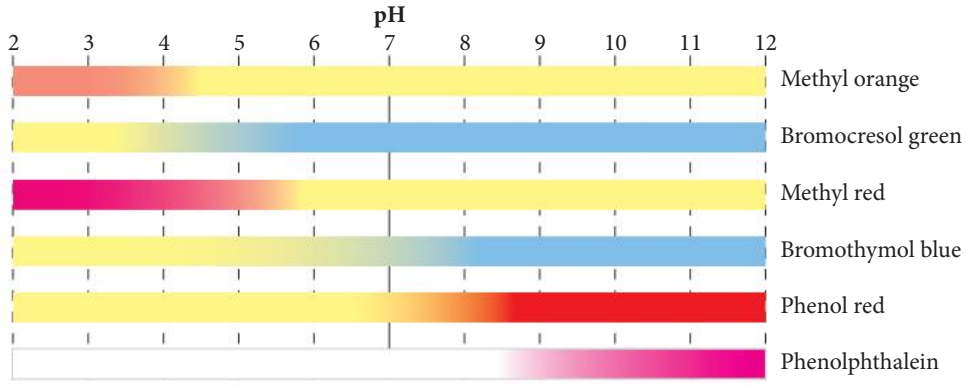
Give examples of when it would be appropriate to use each indicator or a combination of these indicators.

Ideas for improvement or further investigation

1. Outline any areas where you feel that you could adjust your methodology to improve the validity and reliability of your investigation.
2. List any questions that you have after performing this investigation that may involve further investigation.

Table C4.1 Common indicators and their pH ranges

Indicator	Colour change (from low pH to high pH)	pH range
Methyl orange	Red–yellow	3.1–4.4
Bromocresol green	Yellow–blue	3.8–5.4
Methyl red	Pink–yellow	4.4–6.0
Bromothymol blue	Yellow–blue	6.2–7.6
Phenol red	Yellow–red	6.8–8.4
Phenolphthalein	Colourless–red	8.3–10.0



◀ **Figure C4.5** Colours of common indicators over ranges of pH

QUESTION SET 4.1

Remembering

1 Define the following terms.
   - a Volumetric analysis
   - b Accuracy
   - c Parallax error

2 What is used to rinse a burette?

3 Draw a scientific diagram of a volumetric flask.

Understanding

4 Why does universal indicator change colour several times over the pH range 1–14?

5 How can parallax error be minimised?

Analysing

6 A student wanted to fill a burette with hydrochloric acid. He poured some water into the burette, then opened the tap and emptied the burette. The student then filled the burette with hydrochloric acid, adjusted the volume to the zero mark and indicated that he was ready to use the burette. Identify errors in the student's method and justify the correct method for using a burette.

7 A student used three indicators to determine the pH of a sample of water from the local river. The results were colourless in phenolphthalein, yellow in methyl orange and blue in bromothymol blue. Using Figure C4.5, justify whether the sample of river water was acidic, basic or neutral.

Evaluating

8 Methyl orange was used to determine whether some water samples were acidic, basic or neutral. Evaluate the appropriateness of methyl orange for this task.

4.3 Primary standard solutions

To be able to accurately determine the concentration of an unknown solution, it is titrated against a solution with an accurately known concentration. Accuracy is the number of significant figures to which a quantity is known. Some mass balances measure to the nearest gram, while others measure to the nearest milligram (0.001 gram). The mass balance that can measure to the nearest milligram is a more accurate measuring device than the mass balance that measures to the nearest gram. Accuracy is determined by the measuring instrument that is used.

Accuracy is the number of significant figures to which a quantity is known. It is determined by the measuring instrument that is used.

A chemical that can be made up into a solution of accurately known concentration is called a **primary standard**. A primary standard must be stable over a long time and under common laboratory conditions. A primary standard must:

- have a large molar mass so that a reasonable mass is measured; hence, there is a smaller percentage error
- be cheap so that it is affordable for use
- be of high purity so that no side reactions occur
- be stable in the presence of air, so that no reaction with air occurs
- not have any water of hydration, which may change due to atmospheric conditions such as humidity
- dissolve readily in solvent, generally water, to form a stable solution.

Anhydrous sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$) are frequently used as primary standards in school science laboratories since they meet all of these criteria.

EXPERIMENT 4.2

MAKING A PRIMARY STANDARD SOLUTION

Primary standard solutions have an accurately known concentration and are stable over a period of time in common laboratory conditions.

Aim

To make a primary standard solution

Materials

- 250 mL volumetric flask with lid
- Electronic balance
- Clean, dry 150 mL beaker
- Spatula
- Approximately 1.5 g anhydrous sodium carbonate
- 300 mL distilled water
- Wash bottle filled with distilled water
- Filter funnel

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Solid sodium carbonate can irritate skin and eyes.	Wear safety glasses and wash your hands at the end of the experiment.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Rinse the volumetric flask with a small volume of distilled water.
2. Place a clean, dry 150 mL beaker on the electronic balance and tare the balance.
3. Accurately measure out, to the nearest 0.001 g, about 1.4 g of anhydrous sodium carbonate into the beaker.
4. Add about 80 mL of distilled water to the beaker and stir until the sodium carbonate has completely dissolved.
5. Place the filter funnel into the neck of the volumetric flask.
6. Pour the sodium carbonate solution into the volumetric flask.
7. Pour a small volume of distilled water into the beaker, swirl and pour into the volumetric flask.
8. Rinse the filter funnel by pouring some distilled water from the wash bottle into the volumetric flask.
9. Remove the filter funnel.
10. Fill the volumetric flask with distilled water until the bottom of the meniscus is just touching the line on the volumetric flask.
11. Place a lid on the volumetric flask, hold the lid in place, invert and swirl the contents of the flask so that mixing occurs.
12. Label your solution and keep it for use in Experiment 4.3.

Results

Accurately record the mass of anhydrous sodium carbonate that was measured out.

Analysis of results

Calculate the concentration of the sodium carbonate solution. Your answer should be given to four significant figures.

Discussion

1. Justify why the beaker and filter funnel were rinsed after use.
2. Evaluate the accuracy of this technique for preparing a primary standard.
3. Sodium carbonate decahydrate is readily available, has a higher molar mass and is cheaper than anhydrous sodium carbonate. Justify why anhydrous sodium carbonate is used as a primary standard while sodium carbonate decahydrate is not.

QUESTION SET 4.2

Remembering

1. Identify three criteria that must be met for a substance to be used as a primary standard.

Understanding

2. What is the purpose of a primary standard?
3. Explain why sodium hydroxide is not appropriate for use as a primary standard.
4. Use your knowledge of the nature of hydrochloric acid to explain why it should not be used as a primary standard.

Applying

5. A student was making the following primary standard – 250 mL of a 0.135 mol L^{-1} solution of sodium hydrogen carbonate.
   a. Calculate the mass of sodium hydrogen carbonate that must be used to make this solution.
   b. Describe the method used to make this primary standard.

Evaluating

6. A student wanted to measure 90 mL of a solution. Justify whether a 100 mL measuring cylinder or a 100 mL volumetric flask is a more accurate piece of equipment for this task.

4.4 Performing volumetric analysis

The solution in the burette is called the **titrant**. The solution to be analysed – the solution with the unknown concentration – is called the **analyte**.

The most common titration conducted in a school science laboratory is the acid–base titration. The basic technique for performing a titration is as follows:

- One of the solutions will have an accurately known concentration.
- Place one of the solutions in the burette. The acid is generally placed in the burette as bases have the capacity to etch the glass and, over time, change the volume of the burette.
- Use a pipette to transfer a known volume of the other solution to a conical flask that has been rinsed with water.
- Add two drops of an appropriate acid–base indicator (see page 236) to the solution in the conical flask.
- Slowly add the solution from the burette to the conical flask until the indicator just shows the first permanent colour change.
- Record the volume of solution added from the burette.
- Repeat the experiment several times until the volume of solution added from the burette is consistent to within about one-third of a division (0.03 mL). The second and subsequent titrations should involve slowing the rate of flow of solution from the burette to dropwise and parts of drops when near the endpoint. Use the average titre for the most accurately known titrations for your calculations.
- Write a balanced chemical equation and use mole calculations to determine the concentration of the unknown solution.

WORKED EXAMPLE 4.1

Potassium hydrogen phthalate, $KH(C_8H_4O_4)$, is a good primary standard for standardising alkali solutions. It contains one acidic hydrogen per formula unit. Potassium hydrogen phthalate (0.917 g) was dissolved in water and titrated with approximately 0.2 mol L^{-1} sodium hydroxide solution; 27.2 mL hydroxide solution was needed to reach the endpoint. Calculate the accurate molarity of the hydroxide solution.

Answer

$M = 0.165$ mol L^{-1}

Logic

1 Write a balanced chemical equation for the reaction.

$KH(C_8H_4O_4)(aq) + NaOH(aq) \rightarrow Na^+(aq) + K(C_8H_4O_4)^-(aq) + H_2O(l)$

2 Calculate the number of moles of potassium hydrogen phthalate that reacted with the sodium hydroxide.

$$n_{KH(C_8H_4O_4)} = \frac{m_{KH(C_8H_4O_4)}}{M_{KH(C_8H_4O_4)}} = \frac{0.917}{204.22} = 0.00449 \text{ mol}$$

3 Calculate the number of moles of sodium hydroxide that reacted with the potassium hydrogen phthalate.

Using equation $n_{NaOH} = n_{KH(C_8H_4O_4)} = 0.00449$ mol

4 Calculate the molarity of the sodium hydroxide solution.

$$C_{NaOH} = \frac{n_{NaOH}}{V_{NaOH}} = \frac{0.00449}{0.0272} = 0.165 \text{ mol } L^{-1}$$

WORKED EXAMPLE 4.2

The acidity of a particular white wine was determined by titrating 25.0 mL of the wine with 0.0511 mol L^{-1} sodium hydroxide solution; 8.70 mL was required. Calculate the molarity of hydrogen ions in the wine. Assume that the hydrogen ions come entirely from diprotic tartaric acid, $H_2C_4H_4O_6$, and calculate the concentration of tartaric acid in the wine in grams per 100 mL.

Answer

Concentration = 0.133 g/100 mL

Logic

1 Write a balanced chemical equation for the reaction.

$H_2C_4H_4O_6(aq) + 2NaOH\ (aq) \rightarrow 2Na^+(aq) + C_4H_4O_6^{2-}(aq) + 2H_2O(l)$

2 Calculate the number of moles of sodium hydroxide that reacts with tartaric acid.

$n_{NaOH} = C_{NaOH} \times V_{NaOH} = 0.0511 \times 0.00870 = 0.000445\,mol$

3 Calculate the number of moles of hydrogen ions that react with the sodium hydroxide. Using the equation and data in the question: $n_{H^+} = n_{NaOH} = 0.000445\,mol$

Tartaric acid is diprotic; that is, each molecule of tartaric acid contains 2 hydrogen ions.

4 Calculate the molarity of hydrogen ions in tartaric acid.

$$C_{H^+} = \frac{n_{H^+}}{V_{H_2C_4H_4O_6}} = \frac{0.000445}{0.0250} = 0.0178\ mol\ L^{-1}$$

5 Calculate the concentration of tartaric acid in g/100 mL, using equation:

$$n_{H_2C_4H_4O_6} = \frac{1}{2} n_{NaOH} = 0.000222\ mol$$

$$m_{H_2C_4H_4O_6} = n_{H_2C_4H_4O_6} \times M_{H_2C_4H_4O_6} = 0.000222 \times 150.088 = 0.0334\ g$$

$$[H_2C_4H_4O_6] = \frac{m_{H_2C_4H_4O_6}}{V_{H_2C_4H_4O_6}} = \frac{0.0334}{0.0250} = 1.33 g\ L^{-1} = 0.133\ g/100\ mL$$

Try these yourself

a Oxalic acid dihydrate, $(COOH)_2.2H_2O$, can be used as a primary standard for standardising alkali solutions. 0.291 g diprotic oxalic acid required 18.2 mL of a potassium hydroxide solution for exact neutralisation. Calculate the molarity of the hydroxide solution.

b 5.267 g anhydrous sodium carbonate was dissolved in water in a volumetric flask and the volume made up to 250 mL. 10 mL of this solution was pipetted into a conical flask and titrated with hydrochloric acid. 21.3 mL was needed to reach the equivalence point. Calculate the molarity of the hydrochloric acid solution. This solution was then used to determine the concentration of an unknown barium hydroxide solution. 25 mL of the barium hydroxide solution required 27.1 mL hydrochloric acid solution for exact neutralisation. Calculate the molarity of the barium hydroxide solution. In addition, calculate its concentration in grams per litre.

Choice of indicators

It is important that the indicator chosen is appropriate for the pH of the equivalence point. Different acids and bases have different strengths – they have different degrees of ionisation. Hydrochloric acid, sulfuric acid and nitric acid are classified as strong acids because all molecules completely ionise in solution. Other acids are classified as weak acids because only some molecules ionise in solution. Similarly, hydroxide salts and oxide salts are classified as strong bases while most other bases, including carbonates, are classified as weak bases.

As you learnt in *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 7, a reaction between an acid and a base, a neutralisation reaction, is essentially a reaction between the hydronium ions and hydroxide ions to form water:

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$$

or

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

However, during neutralisation reactions, a salt is also formed. When determining which indicator to use, you must:

- identify the salt that is formed
- determine whether either ion in the salt is a weak acid or a weak base or neither
- decide whether the resultant solution will have a pH greater than 7, less than 7 or equal to 7.

In light of this, it is important to choose the most appropriate indicator, the indicator that will change colour at the expected pH of the equivalence point.

Table C4.2 Indicators used for different types of titrations

Type of titration	Example	Predicted equivalence point	Indicator
Strong acid–strong base	Hydrochloric acid and sodium hydroxide	Neutral	Bromothymol blue
Strong acid–weak base	Hydrochloric acid and sodium carbonate	Acidic region	Methyl orange
Weak acid–strong base	Acetic acid and sodium hydroxide	Basic region	Phenolphthalein
Weak acid–weak base	Acetic acid and sodium carbonate	Generally don't use direct titration	

TITRATION – DETERMINING THE ENDPOINT

Visit this website for descriptions, photos and short videos related to performing a titration, especially detecting the endpoint.

WOW

History of volumetric analysis

The French chemist François Antoine Henri Descroizilles made the first burette in 1791. It was further refined by another Frenchman, Joseph Louis Gay-Lussac, who also came up with the names 'pipette' and 'burette' in 1824. In 1855, the German chemist Karl Friedrich Mohr wrote the first book on volumetric analysis titled *Lehrbuch der chemisch-analytischen Titrir-methode* (Instructional Book of Titration Methods in Analytical Chemistry).

Performing the titration

It is now time to put all of this information together and perform a titration.

EXPERIMENT 4.3

PERFORMING A TITRATION

In this titration, you will be using the primary standard that you made in Experiment 4.2 to determine the unknown concentration of a solution of hydrochloric acid. Hydrochloric acid is a strong acid and sodium carbonate is a weak base so the equivalence point will be in the acidic region. Methyl orange is a suitable indicator for this titration.

Aim

To determine the concentration of a hydrochloric acid solution using volumetric analysis

Materials

- 250 mL of an accurately known concentration of sodium carbonate (from Experiment 4.2)
- 50 mL burette
- Retort stand and burette clamp
- 25 mL pipette and pipette filler
- 2 × 150 mL beakers
- 250 mL conical flask
- Dropper bottle containing methyl orange indicator
- 200 mL of hydrochloric acid of unknown concentration
- 2 small labels to label the 150 mL beakers
- Wash bottle with distilled water

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Dilute solutions of hydrochloric acid, sodium carbonate and methyl orange indicator may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Glassware could break and cut your hands.	Keep glassware away from the edge of the bench. When the pipette is not in use, leave the pipette filler on the pipette to prevent it rolling off the bench. If glassware does break, inform your teacher immediately.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Rinse one of the 150 mL beakers with a small amount of the hydrochloric acid solution, empty it, label it and fill it with about 100 mL of the hydrochloric acid solution.
2. Prepare the burette, then fill it with the hydrochloric acid solution.
3. Rinse the other 150 mL beaker with a small amount of the sodium carbonate solution, empty it, label it and fill with about 100 mL of the sodium carbonate solution.
4. Rinse the conical flask with water.
5. Prepare the pipette, then use the pipette to transfer 25.00 mL of the sodium carbonate solution to the conical flask.
6. Add 2 drops of methyl orange indicator to the conical flask and swirl to mix.
7. Place the conical flask under the burette and begin the titration.
8. When the first permanent colour change has occurred, record all results.
9. Repeat the titration several more times until the titrant added is within 0.03 mL.

Results

Record the:

- concentration of sodium carbonate solution
- volume of sodium carbonate used
- volume of hydrochloric acid used.

Analysis of results

1. Calculate the average volume of hydrochloric acid used.
2. Write a balanced chemical equation for the reaction between hydrochloric acid and sodium carbonate.
3. Calculate the number of moles of sodium carbonate placed in the reaction vessel (conical flask).
4. Use the mole ratio from your balanced chemical equation to determine the number of moles of hydrochloric acid that was titrated.
5. Calculate the concentration of hydrochloric acid that was titrated.

Discussion

1. Compare your value for the concentration of the hydrochloric acid with that of other students and with the value provided by your teacher.
2. Discuss any variations in the value and suggest how to improve the accuracy of your results.
3. Justify why the conical flask was rinsed with water and not the solutions that were placed in it.

This is the simplest type of titration – where an acid and a base are titrated directly against each other using an appropriate acid–base indicator. The issues to be considered are:

- identifying the correct indicator to use
- making sure that the chemical equation is correctly balanced to ensure that the correct mole ratio is used in the calculations.

QUESTION SET 4.3

Remembering

1 Identify the term given to a solution that is placed into a burette.

Understanding

2 Justify whether an analyte can be a titrant.

3 Explain why titrations are repeated and the volumes are averaged.

Applying

4 25.00 mL of 0.0873 mol L^{-1} HCl was titrated with 37.30 mL of sodium hydroxide.

- a Identify the most appropriate indicator to be used for this titration.
- b Calculate the concentration of the sodium hydroxide solution.

Analysing

5 20.00 mL of sulfuric acid was titrated with a 0.145 mol L^{-1} solution of sodium hydrogen carbonate. The titration was performed four times. The volumes of sodium hydrogen carbonate were: 22.35 mL, 22.40 mL, 24.35 mL and 22.35 mL.

- a Identify an appropriate indicator to be used in this titration.
- b Justify which solution is in the burette.
- c How will you be able to determine when equivalence has been reached?
- d Write a balanced equation for this reaction.
- e Calculate the concentration of the sulfuric acid solution.

Evaluating

6 A student wanted to use a primary standard of sodium hydrogen carbonate to perform a titration to determine the concentration of acetic acid in a sample of vinegar. The teacher indicated that this was not an appropriate method for this analysis. Explain why this method is inappropriate and make suggestions for improvements to the methodology.

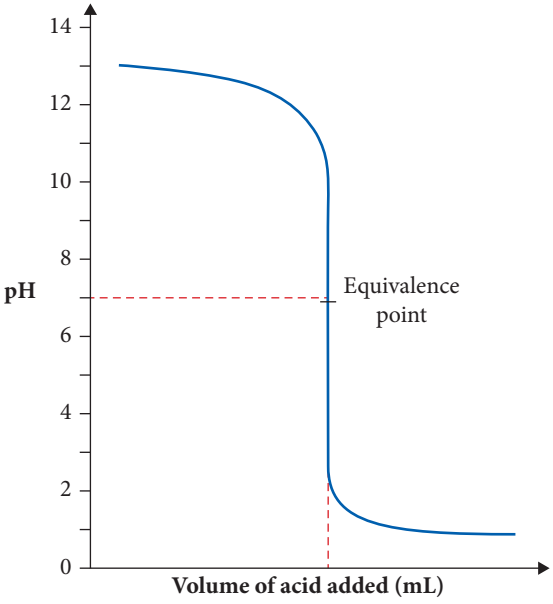
4.5 Other types of titrations

Once the direct titration technique is understood, variations can be used for more complex examples. Some other applications of titrations include:

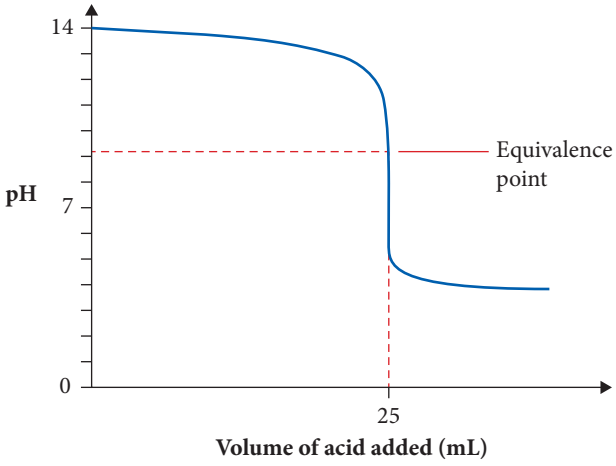
- using pH curves to determine the endpoint
- using back titrations to determine the concentration or mass of a substance that is not able to be determined directly
- performing a redox titration.

Using titration curves

If the solution being analysed is not clear, then it will interfere with the colour change of the indicator. Some solutions, such as malt vinegar and red wine, are so dark that the indicator colour cannot be seen at all. In this case, a pH meter would be used rather than an indicator.



▲ **Figure C4.6** A pH graph for a titration involving a strong base and a strong acid



▲ **Figure C4.7** A pH graph for a titration involving a strong base and a weak acid

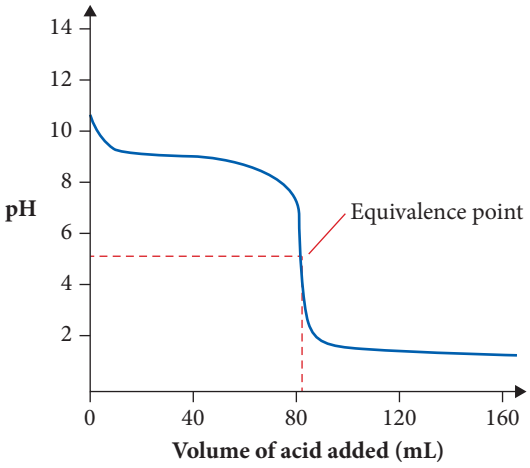
When performing an acid–base titration, the pH of the solution in the reaction vessel changes. If the base is pipetted into the conical flask, then the acid is added from the burette, the pH will change from basic to acidic. The shape of the graph depends on the strength of the acid and base used; however, it is not a linear change.

The graph for a titration of a strong base and strong acid (Figure C4.6) shows that the pH starts at a very high value, in the basic region. It remains fairly constant until close to the equivalence point, when it suddenly decreases. The pH drops from 12–13 to 1–2. When acid is in excess, the pH stays reasonably constant again at a very low pH. The equivalence point is the midpoint of the sudden change in the pH.

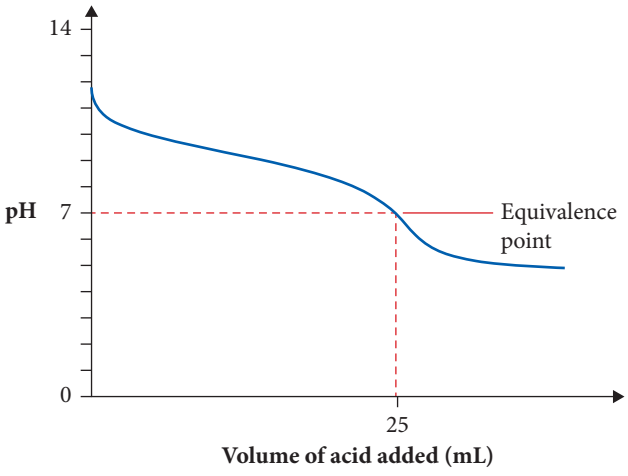
The graph for a titration of a strong base and weak acid (Figure C4.7) again shows that the pH starts at a very high value, in the basic region. It remains fairly constant until close to the equivalence point, when it suddenly decreases, although not as much as for the strong base–strong acid titration. The pH drops from 12–13 to about 4. When acid is in excess, the slope of the pH graph changes and eventually stays reasonably constant at a low pH. The equivalence point is the midpoint of the sudden change in the pH.

The graph for the titration of a weak base and strong acid (Figure C4.8) shows that the pH starts at a high value in the basic region, although not as high as for the strong base. It decreases slightly, and then close to the equivalence point, suddenly decreases, although not as much as for the strong base–strong acid titration. The pH drops from 8–9 to 1–2. When acid is in excess, the pH stays reasonably constant again at a very low pH. The equivalence point is the midpoint of the sudden change in the pH.

The graph for the titration of a weak base and weak acid (Figure C4.9) shows that pH starts at a high value in the basic region, although not as high as for the strong base. It remains fairly constant until close to the equivalence point, when it decreases. This change is much smaller than for the other curves. The pH drops from 8–9 to 4–5. When weak acid is in excess, the pH decreases reasonably constantly at a low pH. Generally, titrations of weak acids and weak bases are not performed directly since the curve does not show a



▲ **Figure C4.8** A pH graph for a titration involving a weak base and a strong acid



▲ **Figure C4.9** A pH graph for a titration involving a weak base and a weak acid

significant change in pH at the equivalence point. It is very difficult to identify the equivalence point.

In large analytical laboratories, these titrations can be done using automated systems. In the school laboratory, it is a little more time consuming. The basic technique is to record the pH in the reaction vessel at the beginning, then again after each millilitre of titrant is added. The data should be analysed so that the location of the large change in pH is identified. The method should be repeated, with pH measurements recorded every 0.2 or even 0.1 mL close to the equivalence point, so that you plot the shape of the graph accurately.

EXPERIMENT 4.4

ACID CONTENT IN ORANGE JUICE

The colour of orange juice distorts the colour change of indicators and makes it difficult to determine the endpoint, so using a pH meter is a more suitable method. It is assumed that all of the acid in the orange juice that reacts in the titration with sodium hydroxide is citric acid ($C_6H_8O_7$). You may need to use a beaker as the reaction vessel since the pH meter may not fit into a conical flask.

Aim

To determine the acid content in orange juice

Materials

- About 20 mL of orange juice (not orange fruit juice drink)
- 200 mL of a standardised sodium hydroxide solution (about 0.1 mol L^{-1})
- Calibrated pH meter
- 50 mL burette
- Retort stand and burette clamp
- 150 mL beaker
- 250 mL conical flask or beaker
- 1 small label to label the 150 mL beaker
- Wash bottle with distilled water

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Dilute solutions of sodium hydroxide may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Glassware could break and cut your hands.	Keep glassware away from the edge of the bench. When the pipette is not in use, leave the pipette filler on the pipette to prevent it rolling off the bench. If glassware does break, inform your teacher immediately.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Rinse the 150 mL beaker with a small amount of the sodium hydroxide solution, empty it, label it and fill it with about 100 mL of the sodium hydroxide solution.
2. Prepare the burette, then fill it with the sodium hydroxide solution.
3. Rinse the reaction vessel (conical flask or 250 mL beaker) with water.
4. Weigh the reaction vessel.
5. Pour about 20 mL of orange juice into the reaction vessel and reweigh it.
6. Add about 50 mL of water to the reaction vessel so the depth is sufficient to cover the glass electrode of the pH meter.
7. Place the pH meter in the reaction vessel and record the pH.
8. Place the reaction vessel under the burette and begin the titration, stopping after each millilitre of sodium hydroxide has been added, to record the pH.

9 Continue adding sodium hydroxide until the pH is fairly constant in the basic region.
10 Repeat the titration a couple more times with more frequent sampling of pH near the large change in pH.

Results

For each titration, record:

- the concentration of sodium hydroxide solution
- a table showing volume of sodium hydroxide added and pH of solution in reaction vessel
- the mass of orange juice added to the reaction vessel.

Analysis of results

1 Write a balanced chemical equation for the reaction between citric acid and sodium hydroxide. Citric acid is a triprotic carboxylic acid.
2 For each dataset except the first, use a spreadsheet program such as Microsoft Excel or Apple Numbers to input the data and produce an *xy* scatter graph of pH versus volume of sodium hydroxide added.
3 Determine the volume of sodium hydroxide added at equivalence.
4 Calculate the number of moles of sodium hydroxide that was titrated with the orange juice.
5 Use the mole ratio from your balanced chemical equation to determine the number of moles of citric acid that reacted with the sodium hydroxide.
6 Calculate the mass of citric acid that reacted with the sodium hydroxide.
7 Calculate the percentage of citric acid present in the orange juice.
8 Average your values for the percentage of citric acid present in the orange juice.

Discussion

1 Compare your value for the percentage of acid in orange juice with those of other students.
2 Discuss any variations in the value and make suggestions for improving the accuracy of your results.
3 Justify why the first dataset was discarded.
4 Justify why the averaging of data occurred only in the last step of the analysis.

Back titrations

Sometimes, it is not appropriate to directly titrate one substance against another. In this instance, the indirect method of **back titration** is used. Back titration is when:

- it is difficult to determine a definite endpoint because the reaction occurs too slowly
- the sample is not soluble in water but will, for example, react with an acid
- the sample is toxic
- the sample is volatile
- the sample is gaseous and in a mixture of gases
- the sample is fairly unreactive; that is, too weak to have a clearly defined endpoint, the sample is present in low concentration or in trace amounts in a mixture.

For examples of back titrations, refer to Context 2, 'Chemical industry', page 52.

A back titration would be used to determine the percentage of calcium carbonate in a sample of limestone. Calcium carbonate is not soluble in water, so the sample cannot be dissolved to form a solution. However, the following reaction will occur with hydrochloric acid:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

A known excess volume of a standardised hydrochloric acid solution would be added to the limestone. It is assumed that the acid only reacts with the calcium carbonate, not with any of the other impurities. The reaction would be left for a period of time and then the reaction vessel would be heated to ensure that the reaction goes to completion and all of the carbon dioxide has been released. A couple of drops of methyl orange indicator are added to the solution, and then it is titrated against a standardised sodium hydroxide solution. The excess hydrochloric acid reacts with the sodium hydroxide until the endpoint is reached. The equation for this reaction is:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

For examples of back titrations in the analysis of wine, refer to Context 1, 'Wine', page 5.

Back titrations are also used for the analysis of the:

- nitrogen content of lawn fertilisers, usually present as ammonium salts
- aspirin (acetylsalicylic acid) content in a commercial painkiller tablet such as Disprin or Aspro Clear
- amount of alcohol in wine.

WORKED EXAMPLE 4.3

a A 2.50 g sample of limestone was dissolved in 75.0 mL of 0.996 mol L^{-1} hydrochloric acid. After heating to ensure that all of the CO_2 was expelled, the solution was cooled and diluted to 250 mL. A 25.0 mL sample of this diluted solution was titrated with 25.27 mL of a standardised solution of 0.1215 mol L^{-1} sodium hydroxide. Determine the percentage of calcium carbonate in the original limestone sample.

b A student wanted to determine the percentage of the ammonium ion, $NH_4^+(aq)$, present in a particular brand of plant food. The student added 50.0 mL of 0.890 mol L^{-1} sodium hydroxide to a 5 g sample of the plant food. This was boiled to promote the formation of ammonia. The excess sodium hydroxide was titrated against 42.3 mL of 0.880 mol L^{-1} hydrochloric acid. Calculate the percentage of ammonium ion present in the plant food.

Answer

a Percentage of calcium carbonate = 88%

Logic

1 Write balanced chemical equations for all reactions.

$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

2 Calculate the original number of moles of HCl that was added to the limestone.

$n_{HCl} = M_{HCl} \times V_{HCl} = 0.996 \times 0.0750 = 0.0747$ mol

3 Calculate the number of moles of HCl that reacted with the NaOH.

$n_{NaOH} = M_{NaOH} \times V_{NaOH} = 0.1215 \times 0.02527 = 0.00307$ mol

$n_{HCl} = n_{NaOH} = 0.00307$ mol

This is the number of moles of unreacted HCl in the 25.0 mL sample of the diluted solution.

Since the solution was 250 mL, the number of moles of HCl present in this solution is 10 times the value calculated above.

$n_{HCl \text{ in } 250 \text{ mL solution}} = 10 \times 0.00307 = 0.0307$ mol

4 Calculate the number of moles of HCl that reacted with the $CaCO_3$.

Number of moles of HCl that reacted with $CaCO_3$ = Number of moles of HCl added − Number of moles of HCl that reacted with NaOH

$n_{HCl \text{ reacted with } CaCO_3} = 0.0747 - 0.0307 = 0.0440$ mol

5 Calculate the number of moles of $CaCO_3$ that reacted with HCl; this is the number of moles of $CaCO_3$ in the limestone sample.

$$n_{CaCO_3} = \frac{1}{2} n_{HCl} = \frac{1}{2} \times 0.0440 = 0.0220 \text{ mol}$$

6 Calculate the percentage of $CaCO_3$ in original limestone sample.

$m_{CaCO_3} = n_{CaCO_3} \times M_{CaCO_3} = 0.0220 \times 100.09 = 2.20$ g

$$\%CaCO_3 = \frac{m_{CaCO_3}}{m_{\text{limestone}}} \times 100 = \frac{2.20}{2.50} \times 100 = 88\%$$

b Percentage of ammonium ion = 2.6%

1 Write balanced chemical equations for all reactions.

$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

2 Calculate the original number of moles of NaOH that was added to the plant food.

$n_{NaOH} = C_{NaOH} \times V_{NaOH} = 0.890 \times 0.0500 = 0.0445$ mol

3 Calculate the number of moles of NaOH that reacted with HCl.

$n_{HCl} = C_{HCl} \times V_{HCl} = 0.881 \times 0.0423 = 0.0373$ mol

$n_{NaOH} = n_{HCl} = 0.0373$ mol

4 Calculate the number of moles of NaOH that reacted with the NH_4^+.

Number of moles of NaOH that reacted with NH_4^+ = Number of moles of NaOH added to plant food − Number of moles of NaOH that reacted with HCl

$n_{NaOH\ reacted\ with\ ammonium} = 0.0445 - 0.0373 = 0.00720$ mol

5 Calculate the number of moles of NH_4^+ that reacted with NaOH; this is the number of moles of NH_4^+ present in the sample of plant food.

From the equation,

$n_{NH_4^+} = n_{OH^-} = 0.00720$ mol

6 Calculate the percentage of NH_4^+ present in the plant food.

$m_{NH_4^+} = n_{NH_4^+} \times M_{NH_4^+} = 0.00720 \times 18.05 = 0.130$ g

$$\%NH_4^+ = \frac{m_{NH_4^+}}{m_{plant\ food}} \times 100 = \frac{0.130}{5.00} \times 100 = 2.6\%$$

Try these yourself

a To calculate the percentage of calcium carbonate in a sample of limestone, a chemist dissolved 0.552 g in 50 mL of 0.121 mol L^{-1} hydrochloric acid, boiled the mixture gently to ensure complete reaction and to expel all carbon dioxide, and then titrated the excess hydrochloric acid with 21.1 mL of 0.0950 mol L^{-1} sodium hydroxide solution. Calculate the mass of calcium carbonate in the sample and hence the percentage.

b To determine the amount of ammonium ion in a sample, a chemist dissolved 0.375 g of the sample in water, added 25 mL of 0.414 mol L^{-1} sodium hydroxide solution and boiled the mixture to drive off all of the ammonia formed. The hydroxide left over, after all of the ammonium ion had been reacted, required 21.2 mL of 0.161 mol L^{-1} hydrochloric acid for exact neutralisation. Calculate the mass of ammonium ion in the original sample and hence the weight percentage of ammonium ion in the sample.

Redox titrations

Volumetric analysis can also be used to analyse redox reactions. As with all titrations, you must determine the equivalence point. When using salts of transition metals such as manganese, the natural colour of their varying oxidation states can be used to determine the endpoint. In other cases, appropriate indicators must be used.

In Experiment 4.5, you will use a redox titration to standardise a potassium permanganate solution. Analytical grade (AR grade) hydrated iron(II) ammonium sulfate, $Fe(NH_4)_2(SO_4)_2.6H_2O$, is a commonly used primary standard for redox titrations. Although it is hydrated, it has a large molar mass and high purity, can be directly weighed, does not react with the atmosphere and remains stable for a long time.

The oxidation reaction is:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

The reduction reaction is:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

Therefore, the reaction for the titration is:

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$



For examples of the use of redox titrations, refer to Context 1, 'Wine', page 5 and Context 2, 'Chemical industry', page 52.

EXPERIMENT 4.5

STANDARDISING POTASSIUM PERMANGANATE

You will use a very pale green solution of hydrated iron(II) ammonium sulfate to determine the concentration of a potassium permanganate solution. The manganese(VII) in MnO_4^- is a purple colour while the manganese(II) is a very pale pink colour. The endpoint is reached when the first permanent pink-purple colour is seen. This indicates a very slight excess of MnO_4^-. However, this one drop of excess MnO_4^- is negligible in the measured volume.

Aim

To standardise a potassium permanganate solution

Materials

- 10 g of hydrated iron ammonium sulfate ($Fe(NH_4)_2(SO_4)_2.6H_2O$)
- 5 mL of concentrated sulfuric acid
- 50 mL of 2 mol L^{-1} sulfuric acid
- 200 mL of unknown concentration of potassium permanganate
- 250 mL volumetric flask and lid
- Filter funnel
- 50 mL burette
- Retort stand and burette clamp
- 25 mL pipette and pipette filler
- Electronic balance
- 10 mL measuring cylinder
- 25 mL measuring cylinder
- 2 × 100 mL beakers
- 250 mL conical flask
- 2 small labels to label the 150 mL beakers
- Wash bottle with distilled water

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Glassware could break and cut your hands.	Keep glassware away from the edge of the bench. When the pipette is not in use, leave the pipette filler on the pipette to prevent it rolling off the bench. If glassware does break, inform your teacher immediately.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Rinse the volumetric flask with a small volume of distilled water.
2. Place a clean, dry 150 mL beaker on the electronic balance and tare the balance.
3. Accurately measure out, to the nearest 0.001 g, about 10 g of hydrated iron(II) ammonium sulfate into the beaker.
4. Add about 80 mL of distilled water to the beaker and stir until the hydrated iron(II) ammonium sulfate has completely dissolved.
5. Place the filter funnel into the neck of the volumetric flask.
6. Pour the iron(II) solution into the volumetric flask.
7. Pour a small volume of distilled water into the beaker, swirl and pour it into the volumetric flask.
8. Add about 5 mL of concentrated sulfuric acid to the volumetric flask.
9. Rinse the filter funnel by pouring some distilled water from the wash bottle into the volumetric flask.
10. Remove the filter funnel.

11 Fill the volumetric flask with distilled water until the bottom of the meniscus is just touching the line on the volumetric flask.
12 Place the lid on the volumetric flask, hold the lid in place, invert, and swirl the contents of the flask so that mixing occurs.
13 Rinse one of the 100 mL beakers with a small amount of the potassium permanganate solution, empty it, label it and fill it with about 100 mL of the potassium permanganate solution.
14 Prepare the burette, then fill it with the potassium permanganate solution.
15 Rinse the other 100 mL beaker with a small amount of the iron(II) solution, empty it, label it and fill it with about 100 mL of the iron(II) solution.
16 Rinse the conical flask with water.
17 Prepare the pipette, then use the pipette to transfer 25.00 mL of the iron(II) solution to the conical flask.
18 Add about 10 mL of 2 mol L^{-1} sulfuric acid solution to the conical flask and swirl to mix.
19 Place the conical flask under the burette and begin the titration.
20 When the first permanent colour change has occurred, record all results.
21 Repeat the titration several more times until the titrant added is within 0.03 mL.

Results

Record the:

- concentration of hydrated iron(II) ammonium sulfate solution
- volume of iron(II) solution used
- volume of potassium permanganate solution used.

Analysis of results

1 Calculate the average volume of potassium permanganate solution used.
2 Calculate the number of moles of iron(II) solution placed in the reaction vessel.
3 Use the mole ratio from your balanced chemical equation to determine the number of moles of permanganate that was titrated.
4 Calculate the concentration of potassium permanganate that was titrated.

Discussion

1 Compare your value for the concentration of the potassium permanganate with those of other students and with the value provided by your teacher.
2 Discuss any variations in the value and make suggestions for improving the accuracy of your results.

Redox titrations are useful for determining the amount of ascorbic acid (vitamin C) in particular foods. A redox titration is used because it specifically targets the ascorbic acid, while an acid–base titration would also react with the other acids present in foods. The ascorbic acid reacts with an iodine solution. Starch is used as the indicator. Redox titrations can also be used to analyse the alcohol (ethanol) content and the sulfur dioxide of wine.

EXPERIMENT 4.6

MEASURING THE CONCENTRATION OF ALCOHOL BY TITRATION

The concentration of alcohol (ethanol) is determined by using a redox back titration. This involves a few steps:

1 The ethanol is oxidised to ethanal (acetaldehyde) by warming a diluted sample of wine with an excess solution of acidified potassium dichromate ($K_2Cr_2O_7$).
$3C_2H_5OH(aq) + Cr_2O_7^{2-}(aq) + 8H^+ \rightarrow 3CH_3CHO(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$
2 Potassium iodide is added to cause the excess dichromate ions to react to form iodine.
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^- \rightarrow 2Cr^{3+}(aq) + 3I_2(aq) + 7H_2O(l)$

3 This iodine is titrated with sodium thiosulfate ($Na_2S_2O_3$).

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^-(aq)$

Aim

To measure the concentration of alcohol by titration

Materials

- 10 mL wine
- 60 mL standard potassium dichromate solution (0.04 M)
- 100 mL standard sodium thiosulfate solution (0.1 M)
- 30 mL of 40% sulfuric acid
- 6 g potassium iodide
- 250 mL distilled water
- Starch indicator (starch solution, freshly made)
- 10 mL pipette
- 2 × 20 mL pipettes
- Pipette filter
- 250 mL volumetric flask
- 3 × 250 mL conical flasks with stoppers
- 10 mL measuring cylinder
- Small funnel
- Burette and stand
- White tile
- Hot water bath
- Thermometer
- Spatula
- Electronic balance

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Sulfuric acid is corrosive.	Wear safety glasses and wash your hands at the end of the experiment.
Iodine solution stains skin, clothing and bench surfaces.	Avoid contact with iodine solution; wear gloves and a lab coat.
Potassium dichromate is a carcinogen.	Avoid exposure to the skin and wear gloves.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1 Pipette 10 mL of wine into a 250 mL volumetric flask.
2 Use distilled water to make the volume up to 250 mL and swirl to mix thoroughly.
3 From this diluted wine, take a 20 mL aliquot and put this in a conical flask.
4 Repeat step 3 twice so that there are three flasks.
5 To each flask add a 20 mL aliquot of 0.04 M potassium dichromate solution.
6 Add 10 mL of 40% sulfuric acid to each flask using a measuring cylinder.
7 Stopper each flask loosely and heat for 10 minutes in a water bath at 45–50°C. Do not allow the water bath temperature to exceed 50°C.
8 After 10 minutes, remove the flasks from the bath and add 2 g of potassium iodide to each flask.
9 Fill a burette with standard thiosulfate solution.
10 Titrate the contents of the flask with the thiosulfate solution. Add 1–2 mL of starch solution when the brown colour of the solution becomes green. The equivalence point of the titration is reached when the blue colour of the starch iodine complex just disappears, leaving a clear green colour.
11 Record the titres for each flask.

Results

Copy and complete the following results table.

Flask	Titre (mL)
1	
2	
3	
Average	

Analysis of results

1. Calculate the number of moles of MnO_4^-(aq) ions in each 20 mL of potassium permanganate.
2. Use the average titre of the standard sodium thiosulfate solution and the number of moles of thiosulfate ions ($S_2O_3^{2-}$) in this titre.
3. Calculate the amount of iodine (I_2) formed during the reaction with the excess permanganate.
4. Use the equation for the reaction between the MnO_4^- and the I^- ions to deduce the amount of MnO_4^- ions in excess after the oxidation of the alcohol.
5. By subtracting the amount of excess MnO_4^- ions from the original amount of MnO_4^- ions added to the diluted wine (calculated in Question **1**), calculate the amount of MnO_4^- ions that reacted with the ethanol.
6. Using the equation for the reaction between the ethanol and the MnO_4^- ions, find the amount of ethanol in each 20 mL aliquot of diluted wine.
7. Calculate the amount of ethanol in the 250 mL volumetric flask.
8. Find the molar mass of ethanol and hence calculate the mass of ethanol in the 10 mL sample of wine.
9. Given that the density of ethanol is 0.785 g mL^{-1}, calculate the volume of ethanol in the 10 mL sample.
10. Determine the percentage alcohol in the wine on a volume/volume basis.

Discussion

Compare your result with the alcohol content as specified by the label on the bottle. If there is a discrepancy between the two, suggest possible reasons for this.

EXPERIMENT 4.7

DETERMINATION OF SULFUR DIOXIDE CONTENT OF WINE

Sulfur dioxide is used in wine making for two reasons. It acts as an antioxidant and as an antimicrobial agent. Unfortunately, some people are allergic to this chemical. There is a legal limit for the total concentration of sulfur dioxide in wine.

Wine must have a concentration of sulfur dioxide of less than 10 mg L^{-1} to be classed as preservative free; otherwise, the wine label must indicate that preservative (220) has been added or that the wine contains sulfites. The maximum level for sulfur dioxide in Australian wine is 300 mg L^{-1}.

Aim

To determine the total mass of sulfur dioxide in wine by performing a redox titration

Materials

- 60 mL of white wine
- 40 mL of 1 M NaOH
- 30 mL of 2 M H_2SO_4
- Starch indicator, freshly prepared
- 100 mL of approximately 0.00500 M iodine
- 20 mL pipette
- Pipette filler

For information about SO_2 levels in wine, refer to Context 1, 'Wine', page 21.

- 3 × 250 mL conical flasks
- 25 mL measuring cylinder
- Small funnel
- Burette and stand
- White tile
- Safety glasses

What are the risks in doing this experiment	How can you manage these risks to stay safe?
Sodium hydroxide and sulfuric acid are corrosive.	Avoid contact with skin. Wear gloves and a lab coat.
SO_2 gas may be produced.	Make sure that the room is well ventilated.
Glassware may be cracked or broken.	Handle glass with care. Inspect and discard any chipped or cracked beakers, no matter how small the damage. Sweep up broken glass with a dustpan and brush; do not use fingers.
Iodine solution stains skin, clothing and bench surfaces.	Avoid contact with iodine solution; wear gloves and a lab coat.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Use a pipette to transfer a 20.00 mL aliquot of wine into each 250 mL conical flask.
2. Add approximately 12 mL of 1 M NaOH to each conical flask and allow to stand for 15 minutes. This releases the SO_2 bound in complex compounds in the wine.
3. Rinse and fill the burette with 0.00500 M iodine solution. Record your initial burette reading and concentration of the iodine.
4. To one flask add approximately 10 mL of 2 M sulfuric acid and 1–2 mL of the starch solution. Immediately titrate the mixture with iodine. Record the burette reading the moment the colour turns permanently blue (endpoint).
5. Repeat the above steps with each of the other two flasks.

Results

1. Calculate the average titre of the iodine solution.
2. Calculate the amount of iodine in moles in the average titre using the concentration of the iodine solution.

Analysis of results

1. Write an ionic equation for the redox reaction that occurs during the titration given the half-equations for the titration reactions are:

   $SO_2(aq) + H_2O(l) \rightarrow 3H^+(aq) + HSO_4^-(aq) + 2e^-$

   $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$
2. Calculate the amount of sulfur dioxide present in each 20.0 mL aliquot of wine.
3. Calculate the amount of sulfur dioxide that would be present in 1 L of wine.
4. Calculate the mass of sulfur dioxide that would be present in 1 L of wine.

Discussion

1. Compare your results with the information on the wine bottle label. Do they agree?
2. Discuss possible sources of error in your result.

Conclusion

Is the wine that you tested within the legal limits for SO_2? What result did you find?

Taking it further

Winemakers may use commercial tests, for example SO_2 ampoules, which determine the concentration of SO_2 in the wine. Investigate the effectiveness of these commercial tests.

QUESTION SET 4.4

Remembering

1 Identify when a back titration may be used.

Understanding

2 Draw a pH curve for a titration between barium hydroxide and acetic acid. The barium hydroxide is in the burette.

3 Some redox titrations do not require the use of an indicator. Explain how the endpoint is determined without the use of an indicator.

4 Why is a pH meter used to determine the endpoint when analysing the citric acid content of orange juice?

Applying

5 A vitamin C tablet, $C_6H_8O_6$, was dissolved in distilled water and made up to a total volume of 250 mL in a volumetric flask. A 25.00 mL aliquot of this solution was titrated against a 0.0200 mol L^{-1} iodine solution, using a starch indicator. On average, 13.10 mL of iodine was used during this titration.

The equation for this reaction is:

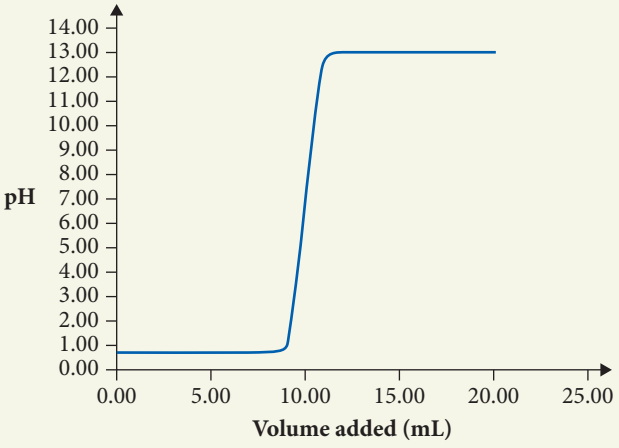
$C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2H^+ + 2I^-$

Calculate the mass of vitamin C in each tablet.

6 Some chemists suspected that their supply of sodium sulfite had been partially converted to sulfate by exposure to air over a long time. To determine the percentage of sulfite in their sample, they dissolved 0.781 g in 50 mL of 0.308 mol L^{-1} hydrochloric acid, boiled the solution gently to expel sulfur dioxide, then titrated the excess hydrochloric acid with 0.144 mol L^{-1} sodium hydroxide solution; 35.4 mL was required. Calculate the percentage of sodium sulfite in the sample.

Analysing

7 A student conducted a titration using 0.060 mol L^{-1} solutions of both acid and base. The results were collected using a pH probe, then graphed. The data is shown on the graph in Figure C4.10.



◀ Figure C4.10

Identify the solution that was placed in the flask at the beginning of the titration, including specific details. Justify your answer.

CHAPTER CHECKLIST

You should know:

- quantitative analysis involves the measurement of numerical data
- the difference between equivalence point and endpoint
- the correct technique for preparing volumetric flasks, pipettes and burettes for use
- the colour changes for common acid–base indicators
- the criteria for a substance to be used as a primary standard:
  - large molar mass
  - cheap
  - high purity
  - stable in the presence of air
  - absence of any water of hydration
  - dissolves readily in solvent
- the correct technique for performing a titration
- how to choose the appropriate indicator for specific types of acid–base titrations
- the shapes of titration curves for different types of acid–base reactions
- the different types of titrations: acid–base titrations, back titrations, redox titrations.

You should be able to:

- use volumetric flasks, pipettes and burettes to measure accurate volumes of solutions
- read volumes accurately without parallax error
- use indicators to classify solutions as acidic, basic or neutral
- prepare a primary standard solution
- calculate the concentration of a solution, given the mass of solute and volume of solution
- perform a titration to obtain valid, reliable and accurate results
- use volumetric analysis to calculate the concentration of an unknown solution using the:
  - concentration of known solution
  - volume of known solution
  - volume of unknown solution
- use pH curves to determine the endpoint of a titration.

CHAPTER GLOSSARY

accuracy depends on the measuring instrument that is used; a mass balance that measures to 0.001 g is a more accurate instrument than a mass balance that measures to 0.1 g

analyte the solution of unknown concentration that will be analysed

back titration a method used to determine the mass or concentration of a substance that is not able to be determined directly

endpoint the physical sign that indicates that the equivalence point has been reached; achieving the correct endpoint depends on using an appropriate method that will undergo a physical change at the appropriate point

equivalence point the point when the reactants are present in the ratio shown by the mole ratio in the balanced chemical equation for the reaction

parallax error an error in measurement due to the observer's position relative to the measuring scale; if the reading is taken at an angle to the scale, then an error is introduced

primary standard a solution of accurately known concentration that remains stable under common laboratory conditions for extended periods of time

titrant the solution in a burette

titration a type of volumetric analysis that determines the equivalence point

volumetric analysis determining the concentration of a sample by measuring the volumes of each reactant that reacts and knowing the concentration of the other reactant

CHAPTER REVIEW QUESTIONS

Remembering

1 Identify the colour change for phenolphthalein indicator.
2 What is the endpoint of a titration?
3 Identify two methods for determining when the endpoint of a titration has been reached.
4 Identify three possible sources of error when using a burette.

Understanding

5 A student performed a titration between sodium hydroxide and a known concentration of sulfuric acid. The student put the sodium hydroxide in the burette and the sulfuric acid was pipetted into the reaction vessel. Prior to using the pipette, the student rinsed it with some distilled water. How would this affect the results?
6 Why is the reaction vessel (conical flask) rinsed with distilled water rather than the solutions used in the titration?
7 Why can phenolphthalein be used to show the endpoint for a titration between a strong acid and a strong base?
8 Justify why anhydrous sodium carbonate can be used as a primary standard.
9 Distinguish between a primary standard solution and a standard solution.

Applying

10 3.25 g of barium hydroxide was used to make 100 mL of solution. 20 mL of this solution was titrated with 17.80 mL of hydrochloric acid.
   a Write a balanced equation for this reaction.
   b Identify an appropriate indicator that can be used for this titration. Justify your answer.
   c Identify the colour change that will occur at the endpoint for the indicator identified in part **b**.
   d Calculate the concentration of the hydrochloric acid solution.
11 25.00 mL of hydrogen peroxide solution was diluted to 250.00 mL using a volumetric flask. 20 mL of the diluted hydrogen peroxide solution was titrated with 19.60 mL of 0.0200 mol L^{-1} acidified potassium permanganate. The equation for this reaction is:

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$

   a Identify the reducing agent in this titration.
   b Outline how the endpoint of this titration will be determined.
   c Calculate the concentration of hydrogen peroxide in the original solution.

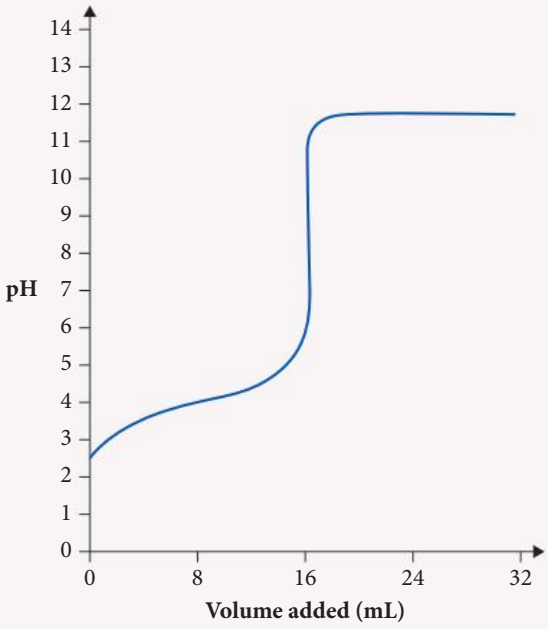
Analysing

12 Look at the pH curve for a titration in Figure C4.11.

- **a** Identify the solution that was pipetted into the reaction vessel.
- **b** Give an example of the type of acid that could have been used in this titration.
- **c** Determine the pH of the endpoint for this titration.

13 A student wanted to determine the nitrogen content, present as NH_4^+, in lawn fertiliser. A 1.432 g sample of the fertiliser was boiled with 25.00 mL of NaOH solution of concentration 1.020 mol L^{-1}. The excess NaOH was titrated against hydrochloric acid of concentration 0.2154 mol L^{-1}, using bromothymol blue indicator. A titre of 19.82 mL was required.

What was the percentage by mass of ammonium ions in the fertiliser?



▲ **Figure C4.11** A pH curve for a titration

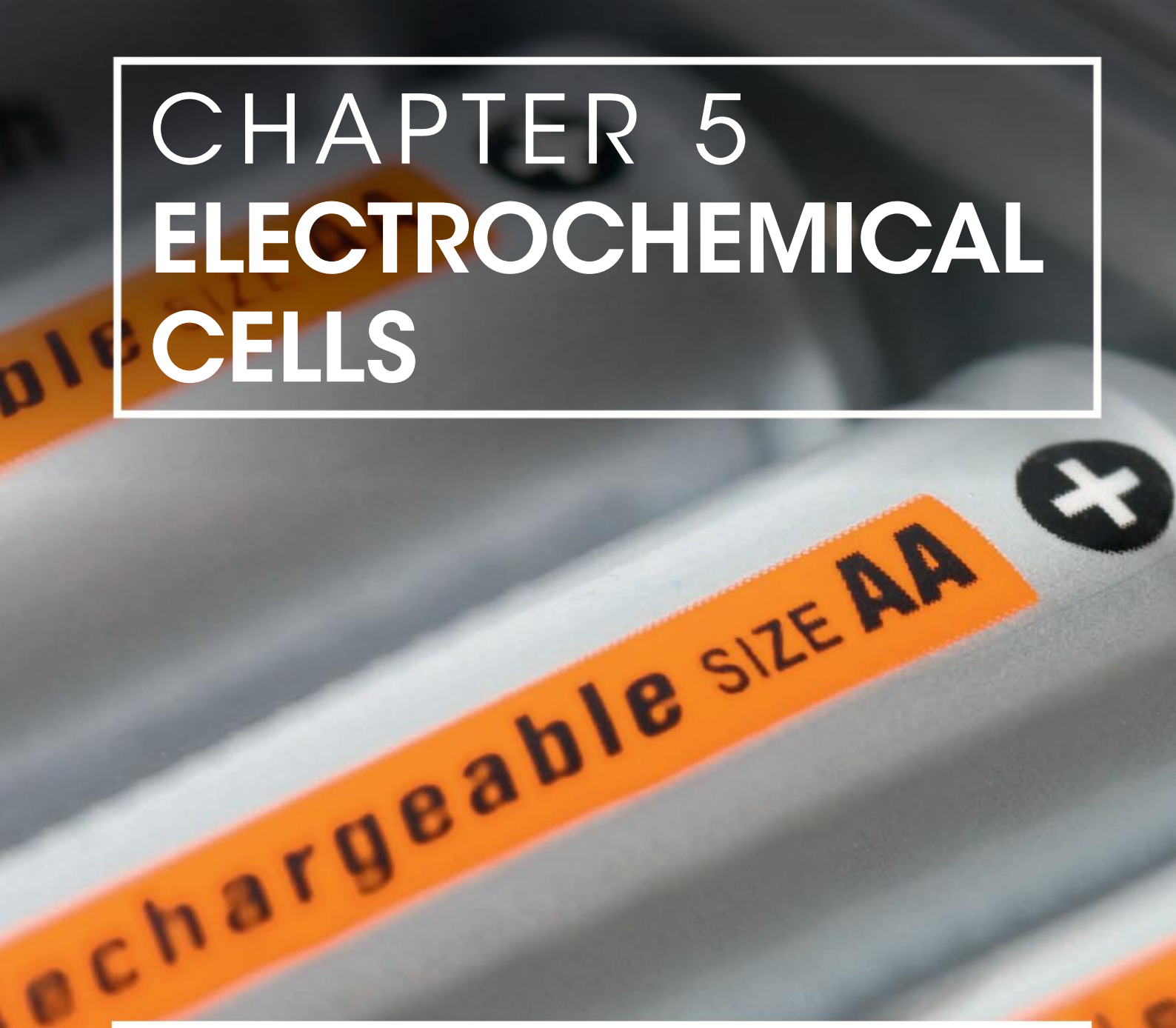
Evaluating

14 Two students were checking the volume in a burette. One student said that the volume was 37.30 mL while the other student said that it was 36.90 mL. Justify why the two students recorded different values.

Reflecting

15 Discuss the usefulness of volumetric analysis as part of a chemist's toolbox.

CHAPTER 5
ELECTROCHEMICAL CELLS



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By the end of this chapter you will have covered the following material.

Science Understanding

- The relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials (ACSCH106)
- Electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction half-reactions connected via an external circuit that allows electrons to move from the anode (oxidation reaction) to the cathode (reduction reaction) (ACSCH107)
- Galvanic cells, including fuel cells, generate an electrical potential difference from a spontaneous redox reaction; they can be represented as cell diagrams including anode and cathode half-equations (ACSCH108)
- Fuel cells can use metal nanoparticles as catalysts to improve the efficiency of energy production (ACSCH109)
- Cell potentials at standard conditions can be calculated from standard electrode potentials; these values can be used to compare cells constructed from different materials (ACSCH110)
- Electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur, and can be used in small-scale and industrial situations (ACSCH111)

5.1 Electrochemical cells

In Chapter 3, the concepts of oxidation and reduction were introduced. It was seen that during oxidation, electrons are released and during reduction, electrons are accepted. Hence, it indicates that there is a movement of electrons. In this chapter, you will learn how this movement of electrons will be harnessed and used to explain how electrochemical cells are utilised.



age fotostock/Alamy

Figure C5.1 ▲ Batteries are galvanic cells.

Electrochemical cells allow for the transformation of energy between chemical potential energy and electrical energy. There are two types of electrochemical cells:

- **Galvanic cells** transform chemical potential energy into electrical energy.
- **Electrolytic cells** transform electrical energy into chemical potential energy.

Galvanic cells are the basis of commonly available batteries. They are also the basis of fuel cells, which are being investigated as alternatives to fossil fuels in powering cars.

The chemistry of electrolytic cells underpins the recharging of rechargeable batteries. Electrolysis is used extensively in the extraction and refining of metals from their ores. Electrolysis is also used in the electroplating industry, where one metal coats another metal – usually a more expensive metal coats a less expensive metal. Electroplating is cheaper than making an object completely from the more expensive metal.



Germany Feng/Shutterstock.com



William Attard McCarthy/Alamy

Figure C5.2 ▲ These copper-plated pots and the chrome-plated wheel rim were made by electroplating.

Applications of both galvanic and electrolytic chemistry are covered extensively in Context 3, 'Alternative sources of energy'. In this chapter, you will learn about the chemistry.

In Chapter 3, you looked at metal displacement reactions and how they are linked to reactivity and oxidation and reduction reactions. Before looking at uses of electrochemical cells, we'll look at another way of comparing the reactivity of different species by introducing the table of standard electrode potentials.

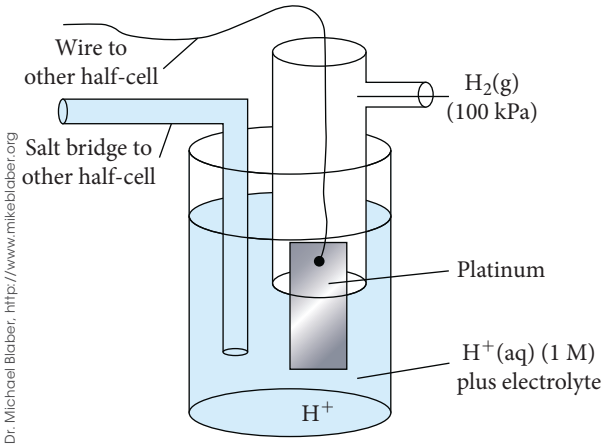
5.2 Standard electrode potentials

In Experiment 3.1, you compared the oxidising strength of a variety of metals when placed in solutions containing cations of other metals. This enabled you to verify the reactivity of different metals. You could continue to perform experiments with different combinations of metals and solutions to put together a table containing their ability to be oxidised for all elements on the periodic table. This would be very time consuming.

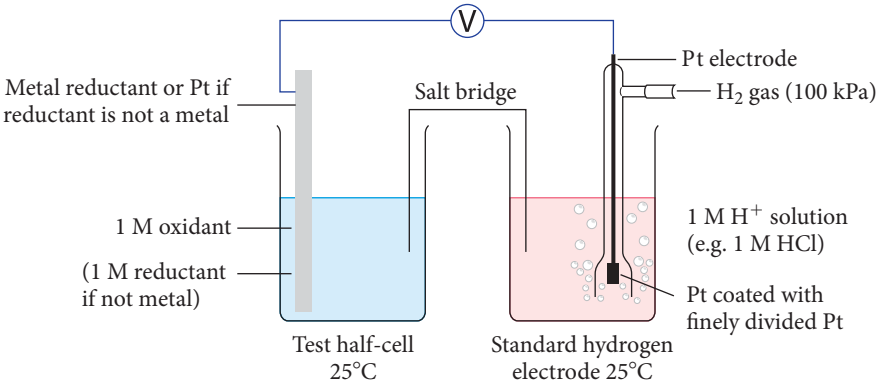
Using a standard to rank oxidising strength

Instead, chemists compare all other species to a reference cell. The reference cell is a hydrogen cell. It contains a solution with hydrogen ions, hydrogen gas and a piece of platinum (called a platinum electrode) to connect this cell to the electric circuit. The hydrogen gas is bubbled into the solution. Platinum is used because it is a good conductor of electricity and it is relatively inert. Therefore, it provides a pathway for the electric charge while not taking part in the chemical reaction.

The test cells consist of a solution containing ions of the element being tested and a metal electrode, or the non-metal with a platinum electrode. The test cell and the reference cell are connected by a **salt bridge** and external wires to a voltmeter. The salt bridge is used to complete the circuit. The simplest salt bridge is composed of a piece of filter paper soaked in an electrolyte such as potassium nitrate, since it will not react with any of the test or reference solutions.
Figure C5.4 shows how this equipment is set up.



▲ **Figure C5.3**
Standard hydrogen cell



Note: 1 M – concentration of 1 mol L^{-1}

◀ **Figure C5.4**
Set-up for determining the standard electrode potentials

Conditions for half-cells

To ensure the validity of the data being collected, standard conditions must be used:

- Solutions must contain 1 mol L^{-1} of ions of the species being tested.
- Solutions must be at 25°C.
- Gases must be at 100 kPa and 25°C.

Determining standard test half-cell potentials

All values are measured relative to the hydrogen half-cell. The hydrogen half-cell is given a value of 0.00 V. Hence, the reading on the voltmeter becomes the value of the test half-cell. This method has been used to produce a table of standard electrode potentials. Table C5.1 shows part of this table for common chemical species.

Elements that are more likely to gain electrons than hydrogen have positive $E°$ values. Elements that are more likely than hydrogen to lose electrons have negative $E°$ values.

Table C5.1 Standard electrode potentials at 25°C

Oxidised form + ne^-	→ Reduced form	E° (V)
$F_2 + 2e^-$	$\rightarrow 2F^-$	+2.87
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	+1.78
$Au^+ + e^-$	$\rightarrow Au$	+1.69
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	+1.51
$PbO_2 + 4H^+ + 2e^-$	$\rightarrow Pb^{2+} + 2H_2O$	+1.46
$Cl_2 + 2e^-$	$\rightarrow 2Cl^-$	+1.36
$O_3 + H_2O + 2e^-$	$\rightarrow O_2 + 2OH^-$	+1.24
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	+1.23
$O_2 + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	+1.23
$MnO_2 + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	+1.22
$Pt^{2+} + 2e^-$	$\rightarrow Pt$	+1.18
$Ag_2O + 2H^+ + 2e^-$	$\rightarrow 2Ag + H_2O$	+1.17
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	+1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO + 2H_2O$	+0.96
$NO_3^- + 3H^+ + 2e^-$	$\rightarrow HNO_2 + H_2O$	+0.93
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	+0.92
$Hg^{2+} + 2e^-$	$\rightarrow Hg$	+0.85
$NO_3^- + 2H^+ + e^-$	$\rightarrow NO_2 + H_2O$	+0.80
$Ag^+ + e^-$	$\rightarrow Ag$	+0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	+0.77
$O_2 + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	+0.70
$MnO_4^- + 2H_2O + 3e^-$	$\rightarrow MnO_2 + 4OH^-$	+0.60
$I_2 + 2e^-$	$\rightarrow 2I^-$	+0.54
$O_2 + 2H_2O + 4e^-$	$\rightarrow 4OH^-$	+0.40
$Ag_2O + H_2O + 2e^-$	$\rightarrow 2Ag + 2OH^-$	+0.34
$Cu^{2+} + 2e^-$	$\rightarrow Cu$	+0.34
$SO_4^{2-} + 4H^+ + 2e^-$	$\rightarrow H_2SO_3 + H_2O$	+0.17
$Sn^{4+} + 2e^-$	$\rightarrow Sn^{2+}$	+0.15
$S + 2H^+ + 2e^-$	$\rightarrow H_2S$	+0.14
$S_4O_6^{2-} + 2e^-$	$\rightarrow 2S_2O_3^{2-}$	+0.08
$2H^+ + 2e^-$	$\rightarrow H_2$	0.00
$Pb^{2+} + 2e^-$	$\rightarrow Pb$	−0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn$	−0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni$	−0.26
$Co^{2+} + 2e^-$	$\rightarrow Co$	−0.28
$PbSO_4 + 2e^-$	$\rightarrow Pb + SO_4^{2-}$	−0.36
$Cd^{2+} + 2e^-$	$\rightarrow Cd$	−0.40
$Fe^{2+} + 2e^-$	$\rightarrow Fe$	−0.45
$2CO_2 + 2H^+ + 2e^-$	$\rightarrow H_2C_2O_4$	−0.49
$Zn^{2+} + 2e^-$	$\rightarrow Zn$	−0.76
$2H_2O + 2e^-$	$\rightarrow H_2 + 2OH^-$	−0.83
$Mn^{2+} + 2e^-$	$\rightarrow Mn$	−1.18
$Al^{3+} + 3e^-$	$\rightarrow Al$	−1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg$	−2.37
$Na^+ + e^-$	$\rightarrow Na$	−2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca$	−2.87
$Ba^{2+} + 2e^-$	$\rightarrow Ba$	−2.91
$K^+ + e^-$	$\rightarrow K$	−2.93
$Li^+ + e^-$	$\rightarrow Li$	−3.04

Oxidising strength increases ↑

Reducing strength increases ↓

State symbols (phase descriptors) have been omitted in order not to clutter up what is already a complex table. All ions are present as aqueous solutions; other substances are present in their stable pure forms at 25°C and 100 kPa.

On the large side arrows, 'oxidising strength' refers to the oxidised form of the redox couple and 'reducing strength' refers to the reduced form of the couple.

The half-reactions are all written in the same format. They are all written as reduction reactions; hence, it is easy to compare their relative strengths as oxidising or reducing agents. In Table C5.1, the magnesium half-equation is near the bottom. The copper half-equation is further up. This indicates that species more likely to be oxidised are at the bottom of the table and species more likely to be reduced are at the top of the table. Hence, the trend as you move down the table is from strong oxidising agents to strong reducing agents.

QUESTION SET 5.1

Remembering

1 Identify the energy transformation that occurs in:
   a a galvanic cell.
   b an electrolytic cell.
2 Identify a use for an electrolytic cell.
3 Identify the conditions under which standard electrode potentials are measured.

Understanding

4 Explain why chemists have used a reference cell to develop the table of standard electrode potentials.

Applying

5 The E° value for the reduction of species A is –1.4 V, while the E° value for species B is +0.70 V. Justify which of species A or B is more likely to be reduced.

5.3 Galvanic cells

In Chapter 3, oxidation and reduction reactions were seen to occur where a metal was in direct contact with a solution containing the ions of a less reactive metal, such as zinc in a copper(II) sulfate solution. The zinc gave up electrons to the copper ions and the products were copper metal and zinc ions. If the reacting species are put into two separate beakers and connected in a specific way, then the same reaction will occur but the electrons can be utilised to do work in the process. This is the principle of galvanic cells. The beaker containing zinc metal and zinc solution is an electrode. The beaker containing the copper metal and the copper(II) solution is the other electrode. Oxidation will occur at one of the electrodes and reduction will occur at the other electrode. These electrodes are given specific names – the electrode where reduction occurs is called the **cathode**, and the electrode where oxidation occurs is the **anode**.



For discussion of different types of batteries, which are examples of galvanic cells, see Context 3, 'Alternative sources of energy', page 64.

Oxidation occurs at the anode while reduction occurs at the cathode.
A mnemonic that will help to remember this is:
Red Cat; An Ox
***Red*uction *Cat*hode; *An*ode *Ox*idation**

Galvanic cells are electrochemical cells in which the oxidation and reduction chemical reactions occur spontaneously. For this to occur, the electrical circuit must be complete. For us to harness and use the electrical energy, the electrons must flow from the anode to the cathode through an external circuit. To do this, the galvanic cell is composed of two half-cells. The simplest half-cells are composed of a solid metal in a solution that contains its ions. The half-cells are in separate beakers so that the electrons can flow through an external circuit rather than transfer by direct contact.

Galvanic cells involve spontaneous reactions. The overall cell voltage is positive.

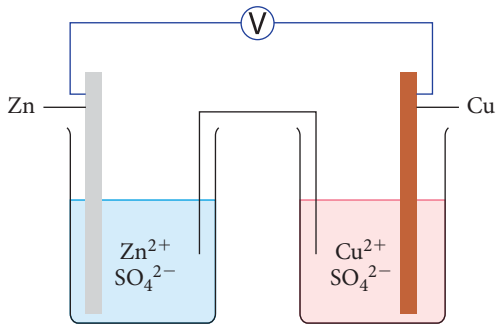


Figure C5.5 ▲ Galvanic cell between zinc and copper

Consider the galvanic cell between zinc and copper. The results of Experiment 3.1 show us that zinc will be the anode and copper will be the cathode. The anode will consist of a solid piece of zinc in a beaker containing a 1 mol L^{-1} solution of zinc ions such as zinc sulfate ($ZnSO_4$). The cathode will consist of a solid piece of copper in a beaker containing a 1 mol L^{-1} solution of copper ions such as copper(II) sulfate ($CuSO_4$). To complete the circuit, a salt bridge and some electrical wires are added. A voltmeter is also included to measure the work done in moving the charge through the circuit. A lamp or ammeter could also be used to show that the charge is moving through the external circuit.

The salt bridge is used to complete the circuit. It can simply be a strip of filter paper soaked in an **electrolyte** such as a potassium nitrate solution. A potassium nitrate solution is commonly used for the salt bridge because it always forms soluble salts when in contact with other solutions. You learnt in *Nelson Chemistry Units 1 & 2* Chapter 7 that all potassium salts are soluble and all nitrate salts are soluble. So when one end of the filter paper with potassium nitrate is placed in the zinc sulfate solution, no precipitate forms. Similarly, when the other end of the salt bridge is in contact with the copper sulfate solution, no precipitate forms. If a precipitate formed, then the circuit would be broken because charge, electrons or ions would not be free to move through that part of the circuit.

At the anode, solid zinc loses electrons to form zinc ions. Over time, the mass of the solid zinc anode decreases. Hence, there is an excess of zinc ions at the anode. The electrons flow through the external circuit to the cathode. The electrons combine with copper ions in the solution to form solid copper. Over time, the mass of the solid copper cathode increases and there becomes an excess of sulfate ions at the cathode. The salt bridge allows for the movement of ions so that the solutions in each beaker remain neutral. Anions flow towards the anode and cations flow towards the cathode to balance charge. There is neither excess cations at the anode nor excess anions at the cathode.

5.4 Using standard electrode potentials to determine cell potentials

Table C5.1 can be used to identify the half-equations for the reactions. Remember, all of the half-equations are written as reduction reactions:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E° = +0.34$ V

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $\quad E° = -0.76$ V

However, there must always be an oxidation reaction and a reduction reaction. Hence, one of the reactions will be reversed. As indicated in the second key concept box on page 257, galvanic cells are spontaneous reactions; hence, they have an overall positive cell voltage. In the metal displacement reactions in Chapter 3, you saw that zinc is more likely to be oxidised and copper is more likely to be reduced. This is supported by the $E°$ values for their half-equations. The reduction of zinc ions to zinc solid has a negative $E°$ value. The $E°$ value for the reduction of Cu^{2+} is bigger than the $E°$ value for the reduction of Zn^{2+}, so the Cu^{2+} will be reduced, and the zinc half-equation will be reversed so that zinc solid oxidises to form zinc ions. The sign for the $E°$ is also reversed:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\quad E° = +0.76$ V

$E°$ is now positive, which indicates that this reaction will occur spontaneously.

$E°$ for the reduction of copper is positive, which indicates that it will occur spontaneously. Therefore, zinc will be oxidised at the anode and copper will be reduced at the cathode:

- Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\quad E° = +0.76$ V
- Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E° = +0.34$ V



For an example of the role of standard electrode potentials in determining the voltage output of commercial batteries, refer to Context 3, 'Alternative sources of energy', page 66.

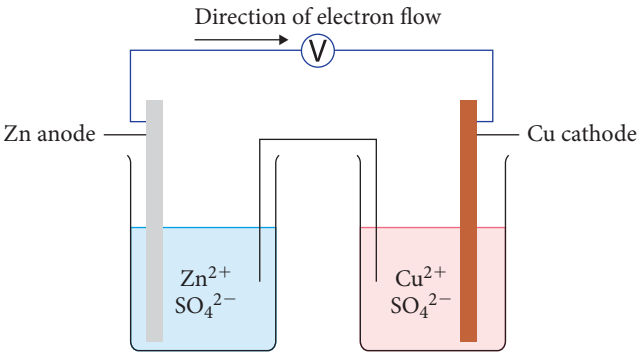
The overall reaction for this galvanic cell can be determined by adding the two equations together. However, before doing this, check that the number of electrons in each half-cell is the same – the number of electrons that is released from the anode is the same as the number of electrons taken in by the cathode – no more, no less. In this example, zinc releases two electrons and copper ions gain two electrons. The electrons are balanced.

Adding the equations together:

$Zn(s) + Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) + Zn^{2+}(aq) + 2e^-$

Since two electrons appear on each side of the equation, they can be cancelled out. The equation becomes:

$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$



▲ **Figure C5.6**
The galvanic cell between zinc and copper

Since the equations are added together, the $E°$ values are also added together:

$(+0.76) + (+0.34) = +1.10\,V$

Hence, the final reaction is written as:

$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq) \quad E° = +1.10\,V$

The positive sign indicates that the reaction occurs spontaneously. In this reaction, energy is transformed from chemical potential energy to electrical energy.

Figure C5.6 shows the copper and zinc cells with the anode, cathode and direction of electron flow through the external circuit clearly labelled.

Sometimes, we may not be able to remember which is the more reactive metal. Hence, we will not be able to work out which metal is most likely to be the anode and undergo oxidation. In this case, the information in the table of standard electrode potentials can be used to determine the anode and cathode reactions.

Consider the galvanic cell with aluminium and tin. One beaker will contain a strip of aluminium and a $1\,mol\,L^{-1}$ aluminium nitrate solution. The other beaker will contain a strip of tin and a $1\,mol\,L^{-1}$ tin(II) nitrate solution. The salt bridge will be a strip of filter paper soaked in potassium nitrate. There are wires from each electrode to a voltmeter to complete the circuit.

This experimental set-up is shown in Figure C5.7.

To use the table of standard electrode potentials, follow these steps:

1 Identify the relevant equations and write them down as they appear in the table.

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \quad E° = -0.14\,V$

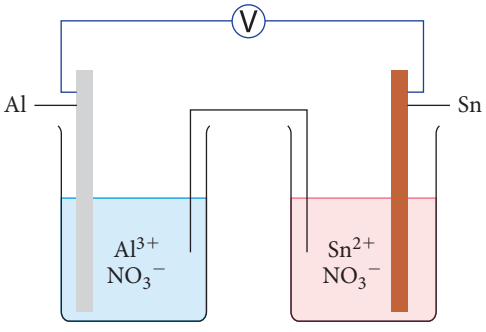
$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \quad E° = -1.66\,V$

2 Galvanic cells consist of an oxidation reaction and a reduction reaction. At present, both equations are written as reduction reactions. So, one of the equations will have to be reversed, but which one? Galvanic cells are spontaneous reactions; therefore, the overall cell voltage must be positive, once the voltages for the two half-cells are added together. Using this information, the aluminium equation will be reversed, so that a positive voltage is achieved when the half-cells are added together. When an equation is reversed, the sign is also reversed.

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \quad E° = -0.14\,V$

$Al(s) \rightarrow Al^{3+}(aq) + 3e^- \quad E° = +1.66\,V$

Aluminium is the anode since it is the oxidation reaction. Tin is the cathode since it is the reduction reaction.



▲ **Figure C5.7**
Set-up of aluminium and tin galvanic cell

3 Before we can add the reactions together, the number of electrons in each equation must be the same. Since 2 and 3 both go into 6, this will be used to balance the electrons. Therefore, the equation for aluminium must be multiplied by 2 and the equation for tin must be multiplied by 3.

When multiplying the equations, the $E°$ values are not multiplied. The $E°$ values give an indication of the difference in electrical potential energy between the two sides of the equation – this does not change when the quantities in the equation change.

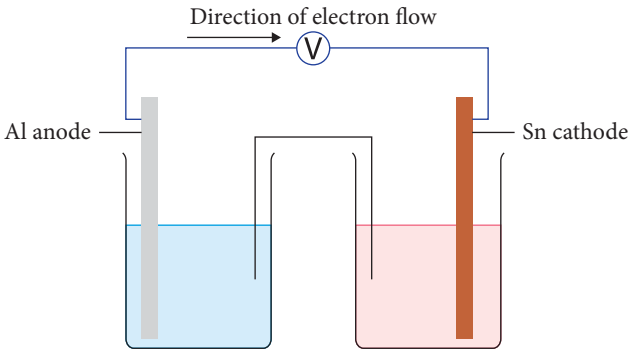


Figure C5.8 ▲ Galvanic cell between aluminium and tin

$3 \times (Sn^{2+}(aq) + 2e^- \rightarrow Sn(s))$ $\quad E° = -0.14$ V

$2 \times (Al(s) \rightarrow Al^{3+}(aq) + 3e^-)$ $\quad E° = +1.66$ V

The equations become:

$3Sn^{2+}(aq) + 6e^- \rightarrow 3Sn(s)$ $\quad E° = -0.14$ V

$2Al(s) \rightarrow 2Al^{3+}(aq) + 6e^-$ $\quad E° = +1.66$ V

The number of electrons being released at the anode is the same as the number of electrons being taken in at the cathode.

4 Cancel the electrons and add the equations and $E°$ values together.

$3Sn^{2+} + 2Al(s) \rightarrow 2Al^{3+} + 3Sn(s)$ $\quad E° = +1.52$ V

Figure C5.8 shows the aluminium and tin cell with the anode, cathode and direction of electron flow through the external circuit clearly labelled.

EXPERIMENT 5.1

CONSTRUCTING GALVANIC CELLS

Galvanic cells involve joining two half-cells by a salt bridge and an external circuit. In this experiment, you will use different combinations of half-cells to determine cell voltages.

Aim

To measure the cell voltage for a variety of galvanic cells

Materials

- 50 mL of 1 mol L^{-1} $CuSO_4$
- 50 mL of 1 mol L^{-1} $MgSO_4$
- 50 mL of 1 mol L^{-1} acidified $FeSO_4$
- 50 mL of 1 mol L^{-1} $ZnSO_4$
- 50 mL of 1 mol L^{-1} KNO_3
- Strip of Cu metal
- Strip of Mg ribbon
- Ungalvanised iron nail
- Strip of zinc metal
- 4 × 100 mL beakers
- Waste bottle for heavy metals
- 7 cm × 7 cm piece of sandpaper
- Voltmeter
- 2 electrical wires with banana plugs on each end
- 2 alligator clips – place one on each electrical wire
- Filter paper cut into strips

- Petri dish
- 4 labels for beakers
- Small piece of Blu-Tack
- Forceps

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Potassium nitrate is a moderately toxic salt.	Use forceps to handle filter paper soaked with potassium nitrate.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Pour 50 mL of each solution into separate labelled beakers.
2. Clean the metals with sandpaper.
3. Stand a piece of metal into the beaker with its corresponding solution so that it is partly submerged. It may be helpful to use a small piece of Blu Tack to hold the metal in place.
4. Soak a piece of filter paper in the petri dish with KNO_3.
5. Place the piece of filter paper so that one end is in the copper(II) solution and the other end is in the zinc solution.
6. Connect the zinc strip and copper strip to the voltmeter with electrical wires.
7. Record the voltage. If the needle drops below zero, connect the wires to the opposite terminals of the voltmeter.
8. Repeat for all other combinations for galvanic cells: copper–magnesium, copper–iron, magnesium–zinc, magnesium–iron and zinc–iron.
9. Dispose of copper(II) sulfate by pouring it into the heavy metals waste bottle. Do not pour it down the drain.

Results

Record the voltage for each galvanic cell in a table.

Analysis of results

1. Which galvanic cell had the largest cell voltage?
2. Which galvanic cell had the smallest cell voltage?
3. For each galvanic cell, identify the anode and the cathode.
4. Use Table C5.1 to determine the theoretical cell voltages for each galvanic cell.
5. Compare your answers to Questions **1–3** with those found by using Table C5.1.

Discussion

Give reasons for any discrepancies between your results and the theoretical values obtained from Table 5.1.

Other simple galvanic cells

Galvanic cells can also be produced by using electrodes that have an inert conductor, such as platinum metal or a graphite rod, in a beaker that contains a:

- mixture of solutions of a metal with varying oxidation states, such as $Sn^{2+}(aq)$ and $Sn^{4+}(aq)$
- gas being bubbled in and ions of that gas (see Figure C5.3).

WORKED EXAMPLE 5.1

A galvanic cell was made by combining a $Cl_2(g)$, $Cl^-(aq)$ electrode with a $Sn^{2+}(aq)$, $Sn^{4+}(aq)$ electrode as shown in Figure C5.9. Determine the anode, cathode, cell voltage and direction of electron flow.

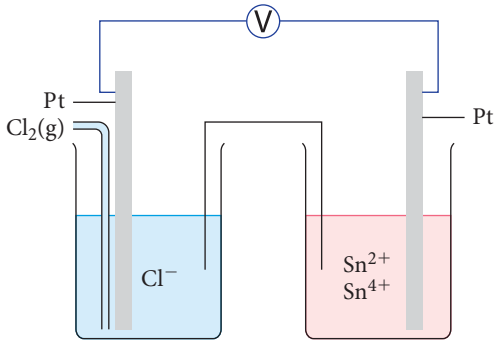


Figure C5.9 ▶ Galvanic cell using inert electrodes in chloride and tin solutions

Answer

The platinum electrode in the tin solutions is the anode.

The platinum electrode in the chloride solution with chlorine bubbled through it is the cathode.

The cell voltage is +1.21 V.

The electron flow is through the external circuit from the platinum wire in the tin solutions to the platinum wire in the chloride solution with chlorine bubbled through it.

Logic

1 Decide on the oxidation reaction and reverse that equation. In this case, the tin equation will be reversed, so that a positive voltage is achieved when the half-cells are added together. Remember to reverse the sign too.

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $\quad E° = +1.36$ V

$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$ $\quad E° = -0.15$ V

The chlorine reaction occurs at the cathode because it is the reduction reaction. The tin reaction occurs at the anode because it is the oxidation reaction.

2 Before you add the reactions together, check that the number of electrons in each equation is the same. Both equations have 2 electrons.

3 Cancel the electrons and add the equations and $E°$ values together.

$Cl_2(g) + Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2Cl^-$ $\quad E° = +1.21$ V

Try these yourself

Determine the anode, cathode, direction of electron flow and cell voltage for the galvanic cell between:

a $Fe^{2+}(aq)$, $Fe^{3+}(aq)$ and $Mg(s)$, $Mg^{2+}(aq)$.

b $H_2(g)$, $H^+(aq)$ and $Ag(s)$, $Ag^+(aq)$.

Using cell notation to represent galvanic cells

Chemical formulas are used to represent the names of chemicals. Rules have been developed so that everyone understands which compound is represented by which chemical formula; for example, water is represented by the formula H_2O. Similarly, chemists use cell notation to represent electrochemical cells. The rules for writing cell notation are:

- The anode reaction is always written on the left of the salt bridge.
- The cathode reaction is always written on the right of the salt bridge.
- The electrodes always appear on the far left and the far right of the notation.
- Different phases are separated by a single vertical line |.
- The salt bridge is represented by a double vertical line ||.
- Species of the same phase are separated with a comma.

WORKED EXAMPLE 5.2

a Use the rules for writing cell notation to represent the galvanic cell in Figure C5.8.

b Use the rules for writing cell notation to represent the galvanic cell in Figure C5.9. Both cells contain inert electrodes so remember to include them in your cell notation.

Answers

a $Al(s) \mid Al^{3+}(aq) \mid\mid Sn^{2+}(aq) \mid Sn(s)$

b $Pt(s) \mid Sn^{2+}(aq), Sn^{4+}(aq) \mid\mid Cl_2(g) \mid Cl^-(aq) \mid Pt(s)$

Logic

1 The anode: The aluminium half-reaction occurs at the anode so is written on the left side of the salt bridge. The aluminium electrode is written on the far left and the aluminium metal is separated from the aluminium ions by a single vertical line since they are different phases. Hence, the aluminium half-reaction is represented as: $Al(s) \mid Al^{3+}(aq)$

2 The cathode: The tin half-reaction occurs at the cathode so is written on the right side of the salt bridge. The tin electrode is written on the far right and the tin metal is separated from the tin(II) ions by a single vertical line since they are different phases. Hence, the tin half-reaction is represented as: $Sn^{2+}(aq) \mid Sn(s)$

3 Putting it together, including the salt bridge: The aluminium half-reaction occurs at the anode so is written on the left side of the salt bridge. The tin half-reaction occurs at the cathode so is written on the right side of the salt bridge. The galvanic cell is represented as:

$Al(s) \mid Al^{3+}(aq) \mid\mid Sn^{2+}(aq) \mid Sn(s)$

1 The anode: The oxidation of tin(II) to tin(IV) occurs at the anode, so this is written on the left side of the salt bridge. The platinum electrode is written on the far left and separated by a single vertical line from the tin ions since it is a different phase. The tin(II) and tin(IV) ions both have the same phase, so they are separated by a comma. The tin half-reaction is written as:

$Pt(s) \mid Sn^{2+}(aq), Sn^{4+}(aq)$

2 The cathode: The reduction of chlorine to chloride ions occurs at the cathode, so this is written on the right side of the salt bridge. The platinum electrode is written on the far right. The platinum electrode, the chlorine gas and the chloride ions are each separated by a single vertical line since they are all different phases. The chlorine half-reaction is written as:

$Cl_2(g) \mid Cl^-(aq) \mid Pt(s)$

3 Putting it together, including the salt bridge: The tin half-reaction occurs at the anode so is written on the left side of the salt bridge. The chlorine half-reaction occurs at the cathode so is written on the right side of the salt bridge. The galvanic cell is represented as:

$Pt(s) \mid Sn^{2+}(aq), Sn^{4+}(aq) \mid\mid Cl_2(g) \mid Cl^-(aq) \mid Pt(s)$

Try these yourself

Use cell notation to represent the galvanic cell between:

a $Fe^{2+}(aq)$, $Fe^{3+}(aq)$ and $Mg(s)$, $Mg^{2+}(aq)$.

b $H_2(g)$, $H^+(aq)$ and $Ag(s)$, $Ag^+(aq)$.

QUESTION SET 5.2

Remembering

1 Define:
   a galvanic cell.
   b salt bridge.
2 List the four steps required to determine the cell voltage for a galvanic cell and to write its overall cell equation.

Understanding

3 Mathematically, how can you tell that there is a spontaneous chemical reaction occurring in a galvanic cell?
4 Use Table C5.1 to determine the $E°$ value for the following half-equations:
   a $Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$
   b $Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$
   c $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
5 Explain why the blue solution decolourises when a galvanic cell is set up using a strip of copper in a copper(II) solution and a strip of lead in a lead(II) nitrate solution.

Applying

6 Draw a galvanic cell for each of the following, clearly indicating the anode, cathode and direction of electron flow.
   a A strip of tin in a solution of tin(II) chloride and a strip of zinc in a solution of zinc sulfate.
   b A platinum wire in a solution of potassium chloride with chlorine being bubbled in and a strip of cobalt in a cobalt(II) chloride solution.
7 Determine the overall equation and cell voltage for a galvanic cell consisting of:
   a an iron nail in an iron(II) chloride solution and a silver wire in a silver nitrate solution. The two half-cells are joined by a potassium nitrate salt bridge and an external circuit.
   b a platinum wire in a solution of iodine and potassium iodide and a platinum wire in a solution containing both iron(II) and iron(III) ions. The two half-cells are joined by a potassium nitrate salt bridge and an external circuit.
8 Represent each of the galvanic cells in Question 7 using cell notation.

Analysing

9 Justify whether each of the following will produce galvanic cells.
   a $2Ag(s) + Pb^{2+}(aq) \rightarrow Pb(s) + 2Ag^+(aq)$
   b $2Cl^-(aq) + Zn^{2+}(aq) \rightarrow Zn(s) + Cl_2(g)$
   c $Ni(s) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + Ni^{2+}(aq)$

5.5 Fuel cells

When we think of fuels as a source of energy, we think of the combustion reactions where chemical energy is converted to heat energy. However, a **fuel cell** is an electrochemical device. It converts chemical energy directly into electrical energy, without the need for any combustion reactions. Since a fuel cell is a type of galvanic cell, it has the same structure as described above – an anode, a cathode, an electrolyte and the flow of electrons through an external circuit.

The most commonly used fuel in a fuel cell is hydrogen, although short-chain alkanes have also been used. One way a fuel cell is different from a normal galvanic cell is that the fuel and air are continuously fed into the cell – the electrodes don't need to be replaced.

In most fuel cells, hydrogen is oxidised at the anode and oxygen is reduced at the cathode. A by-product of the fuel cell is the production of water.

FUEL CELL ANIMATION

View the animation of the operation of a fuel cell.

The reactions in the fuel cell are:

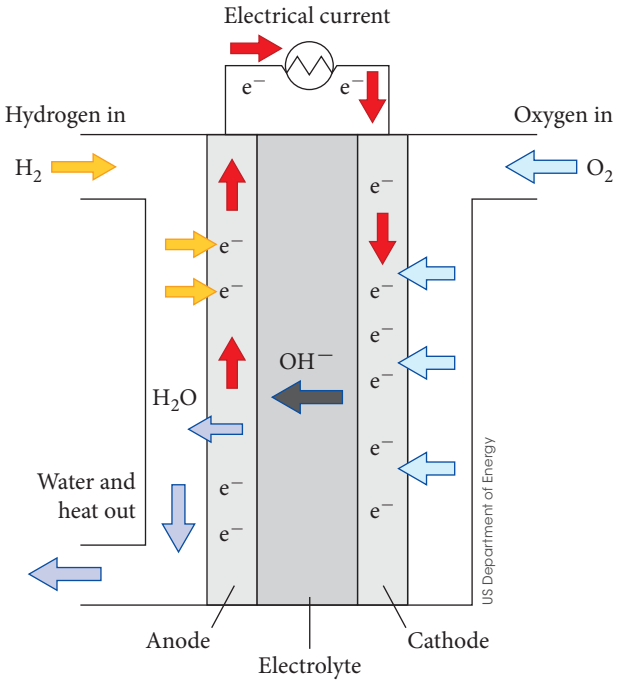
$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \qquad E^\circ = +0.40\ V$$

$$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^- \qquad E^\circ = +0.83\ V$$

Different types of fuel cells generally differ in the type of electrolyte used. For example, the alkali fuel cell uses a concentrated potassium hydroxide electrolyte.

The fuel cell is compartmentalised. The hydrogen and oxygen are on opposite sides with the electrolyte in the middle compartment. The electrodes are porous to allow the gas molecules to pass through. They are lined with a catalyst that assists with the breaking of bonds in the gaseous molecules. The most commonly used catalyst is platinum, although rhodium and nickel are also used. The use of a platinum catalyst is one of the main costs of a fuel cell.

Fuel cells can be stacked together to increase the total cell voltage, just as batteries are added in series to increase the total voltage output. The water produced must be removed from the cell; otherwise, the electrolyte will become diluted, which will affect the efficiency of the cell.



▲ **Figure C5.10**
Alkali fuel cell

Metal nanomaterials in fuel cells

The platinum catalyst contributes significantly to the cost of developing a fuel cell. Therefore, scientists have focused their research on trying to develop more efficient and cheaper catalysts. In *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 9, you learnt that catalysts increase the rate of a chemical reaction, without taking part in the reaction. You also learnt that surface area affects the rate of a chemical reaction. Scientists have investigated ways of increasing the surface area of the catalyst in fuel cells. This has involved the use of nanoparticles. Nanoparticles have a size of about one-billionth of a metre. Lining the electrodes with many nanoparticles instead of a larger piece of platinum will increase the surface area of the catalyst. This will allow the bonds of more molecules of hydrogen and oxygen to be broken at any particular time, which increases the rate of the reaction of the fuel cell.

The other area of research is the use of materials other than platinum as the catalyst in fuel cells. Mixed metal nanoparticles using a nanostructure support composed of carbon have been investigated. One such mixed metal nanoparticle is composed of platinum and ruthenium.

For more information about fuel cells, refer to Context 3, 'Alternative sources of energy', page 74, and Context 6, 'Molecular manufacturing', page 138.

WOW

Recharging fuel cells

Another area of research is the recharging of fuel cells when used in cars. Refuelling stations involve storage of hydrogen gas in tanks at a pressure of 691 atm. To achieve these pressures, high-pressure pumps are needed to fill the tanks. These pumps use a lot of energy.

An alternative storage mechanism is for hydrogen to be absorbed at high densities onto the surface of magnesium. However, the release of hydrogen from the magnesium surface is a very slow process. Researchers in The Netherlands are investigating the use of layers of magnesium and titanium for storage of hydrogen. They have found that the thinner the layers, the faster the hydrogen is released. This suggests that it may be beneficial to investigate the use of a matrix of nanoparticles of these metals for storage of hydrogen at refuelling stations.

PUBLIC LECTURE – A BLUEPRINT FOR NEW FUEL CELL CATALYSTS

Watch this video of Daniel Freibel from SLAC National Accelerator Centre, Stanford University, talking about new fuel cell catalysts.

QUESTION SET 5.3

Remembering

1 What is a fuel cell?
2 Identify the energy transformation that occurs in a fuel cell.
3 What is a catalyst?
4 Identify the most common catalyst used in fuel cells.

Understanding

5 A fuel cell releases only a small voltage. How can this be used to provide the energy for a car?
6 Describe the chemistry of a fuel cell.

Reflecting

7 Discuss some of the current issues related to the use of fuel cells and the research that is being undertaken to address these issues.
8 Discuss the impact of the use of fuel cells on society and the environment.



For more information about batteries and recharging batteries, refer to Context 3, 'Alternative sources of energy', page 67.

5.6 Electrolytic cells

During electrolysis, electrical energy is converted to chemical potential energy. Since electrical energy is used to produce a chemical reaction, it is not spontaneous. Electrolysis is used to force chemical reactions to occur. Batteries are galvanic cells – they convert chemical energy to electrical energy. However, in rechargeable batteries, these reactions can be reversed by applying a voltage to the battery. Recharging batteries involves converting electrical energy to chemical energy.

Electrolysis is used in the mining industry when metals are extracted from their ores. The metals are the valuable commodities, not the ores. Hence, the industrial process of electrolysis is used to extract the metal.

Most metals are not found in their pure form. They are found in mineral compounds. Examples of common metals and the minerals from which they are extracted are given in Table C5.2.



For more information about the use of electrolysis in industrial processes, refer to Context 2, 'Chemical industry', page 38.

Table C5.2 Common metals and some of their minerals

Metal	Name and formula of mineral
Copper	Chalcopyrite, $CuFeS_2$, and malachite, $Cu_2(CO_3)(OH)_2$
Iron	Haematite, Fe_2O_3
Zinc	Sphalerite, (Zn,Fe)S
Silver	Argentite, Ag_2S
Aluminium	Generally bauxite, which is a mixture of gibbsite, $Al_2O_3.3H_2O$, and boehmite, $Al_2O_3.H_2O$
Lead	Galena, PbS

Therefore, to extract the metal from the ore, it has to undergo several physical and chemical processes (see *Nelson Chemistry Units 1 & 2* Context 2). These processes usually do not occur spontaneously; energy has to be put in to force them to occur. One of the chemical processes used is electrolysis. Electrolytic cells can be constructed in a single container – the two half-reactions are able to occur in the single container, since it is the anions and cations in the ionic compound or solution that are undergoing the reaction.

EXPERIMENT 5.2

EXTRACTION OF COPPER BY ELECTROLYSIS

Copper carbonate powder will be used as the copper mineral. Copper carbonate is not soluble in water, so sulfuric acid is used to get copper into solution. Electrolysis is used on the resulting copper(II) sulfate solution to produce copper metal.

Aim

To extract copper from copper(II) carbonate by using electrolysis

Materials

- 6 g copper(II) carbonate powder, $CuCO_3$
- Spatula
- Electronic balance
- 50 mL of 1 mol L^{-1} sulfuric acid, H_2SO_4
- 100 mL beaker
- 2 graphite electrodes
- Small piece of Blu-Tack
- Powerpack
- 2 electrical wires with banana plugs
- 2 alligator clips, one to be placed on each electrical wire
- Waste bottle for heavy metals

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.

In your write-up, add any more risks you can think of, as well as ways to manage them.

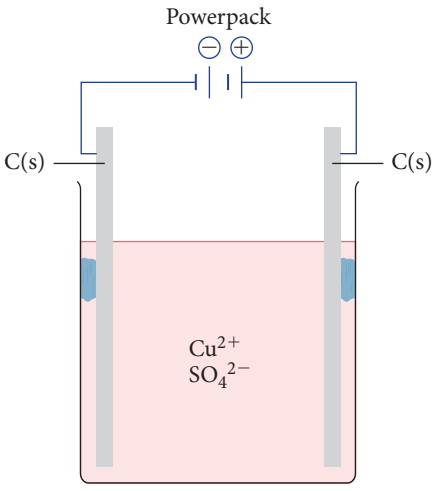
Procedure

Part A

1. Weigh out about 6 g of copper(II) carbonate into the 150 mL beaker.
2. Pour about 50 mL of 1 mol L^{-1} sulfuric acid into the beaker and stir it.
3. Record your observations.

Part B

4. Stand the two graphite electrodes in the beaker, securing them to the side with Blu-Tack, as shown in Figure C5.11.
5. Attach the electrical wires to the electrodes and to the DC terminals of the powerpack.
6. Set powerpack to 6 V and turn it on.
7. Record your observations.
8. Dispose of the copper(II) sulfate by pouring it into the heavy metals waste bottle. Do not pour it down the drain.



▲ **Figure C5.11** Set-up for electrolysis of copper

Results

Record all observations for both parts of the experiment.

Analysis of results

1. How could you tell that a chemical reaction occurred when sulfuric acid was added to copper(II) carbonate?
2. Write a balanced equation for the reaction that occurred when sulfuric acid was added to copper(II) carbonate.
3. How could you tell that a chemical reaction occurred when the copper(II) solution was electrolysed?
4. Write a half-equation for the reduction of the copper(II) ions in solution.

Discussion

1. Discuss how you could tell when the reaction had gone to completion.
2. How could you have increased the rate at which the electrolysis reaction occurred?
3. Why did the powerpack need to be set to 6 V? Would this reaction have occurred at a lower voltage?

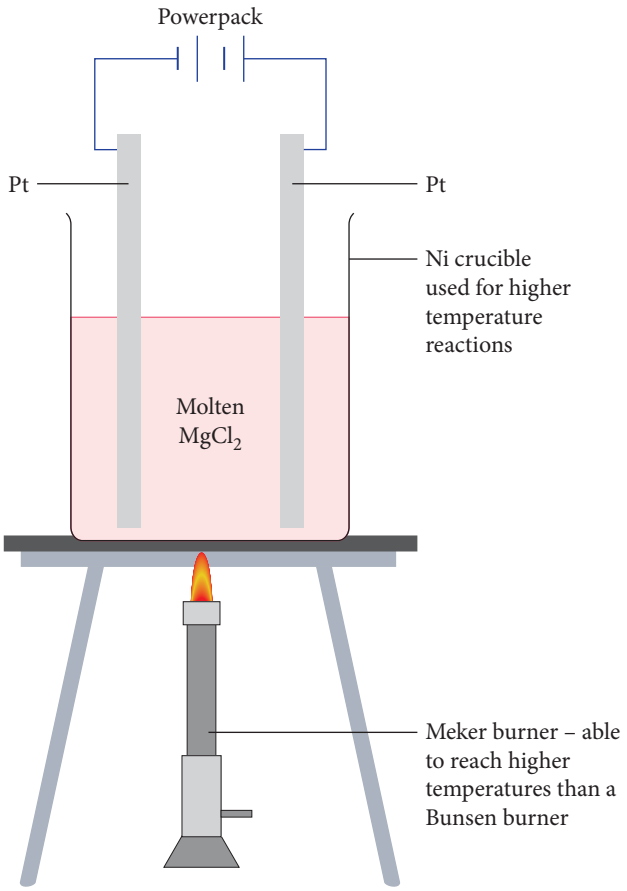


Figure C5.12 ▲ Set-up for electrolysis of molten magnesium chloride

In Experiment 5.2, you saw an electrolysis reaction where one of the products was copper metal. While it is a simple experiment to perform, there is a great deal of chemistry to be understood. An aqueous solution of a copper salt was used. This contains some complex chemistry due to the presence of water, so we will start the explanation of electrolysis using molten salts.

Electrolysis of molten salts

Molten salts are the liquid form of ionic compounds, such as magnesium chloride. This requires temperatures above 700°C, much higher than can be achieved in a school laboratory. The melting point of magnesium chloride is 714°C. However, the advantage of using molten salts is that there are no competing reactions occurring. This is the method used industrially for extracting magnesium and sodium from their salts.

Molten magnesium chloride contains Mg^{2+} and Cl^- ions, so these are the reactants for electrolysis. Electrolysis is an electrochemical reaction, so there must be an anode reaction and a cathode reaction. Oxidation occurs at the anode and reduction occurs at the cathode.

- Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
- Cathode: $Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$

We can use Table C5.1 to find the $E°$ values for these half-equations.

- Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$ $\quad E° = -1.36$ V
- Cathode: $Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$ $\quad E° = -2.37$ V

The electrons are balanced, and the equations and $E°$ values are added together to determine the overall equation and voltage for this electrolytic cell.

- Overall reaction: $Mg^{2+}(l) + 2Cl^-(l) \rightarrow Cl_2(g) + Mg(l)$ $\quad E° = -3.73$ V

The negative sign for the voltage indicates that this is not a spontaneous reaction. This is the approximate voltage that must be applied to the system; that is, provided by a battery or powerpack. Since the species present are not in standard conditions, this voltage is a guide only.

Electrolysis of aqueous solutions

Aqueous solutions contain ionic salts dissolved in water. Hence, an advantage of these electrolysis reactions over electrolysis of molten salts is that they can occur at room temperature. Although the set-up is a bit more straightforward, the chemistry is a little more complicated because as well as the ions in the electrolyte, water is also present and it could be electrolysed instead of the ions. There are competing reactions occurring and you need to be able to determine which is the main reaction occurring at each electrode.

Three factors need to be considered when determining which chemical reaction occurs at the anode and cathode:

- nature of the electrolyte
- concentration of the electrolyte
- nature of the electrode.

Nature of an electrolyte

The electrolyte is the solution that is used in the electrolytic cell. Different solutions have different ions, which have different $E°$ values for their half-equations. The water could also be oxidised at the anode and/or reduced at the cathode. We will use Table C5.1 to assist with understanding the chemistry. To ensure that we are only investigating the effect of the nature of the electrolyte, the other factors must be kept constant. Therefore, the concentration of solution for all examples will be kept constant and the electrodes will be kept constant. Graphite electrodes will be used for each of these examples. Graphite electrodes are used in school experiments because they conduct electricity, they do not take part in the reaction (they are inert) and they are relatively cheap.

Consider a solution of copper(II) bromide, $CuBr_2$. The ions $Cu^{2+}(aq)$ and $Br^-(aq)$ are present since it is a solution. The half-equations for these ions can be determined from Table C5.1.

- Oxidation: $2Br^-(aq) \rightarrow Br_2(l) + 2e^-$ $\quad E° = -1.09$ V
- Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E° = +0.34$ V

However, as stated earlier, water is also present. When water is electrolysed, it decomposes to form hydrogen gas and oxygen gas. The half-equations for the oxidation and reduction of water to form oxygen and hydrogen, respectively, can be determined from Table C5.1.

- Oxidation: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E° = -1.23$ V
- Reduction: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad E° = -0.83$ V

Therefore, there are two possible oxidation reactions at the anode:

$$2Br^-(aq) \rightarrow Br_2(l) + 2e^- \qquad E° = -1.09 \text{ V}$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E° = -1.23 \text{ V}$$

There are also two possible reduction reactions at the cathode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E° = +0.34 \text{ V}$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83 \text{ V}$$

The reaction that is more likely to occur is the one that requires the least input of energy; that is, the least negative voltage.

- At the anode, the preferred reaction is the oxidation of the bromide ions since its voltage is less negative than that for the oxidation of water.
- At the cathode, the preferred reaction is the reduction of copper since its voltage is less negative than that for the reduction of water.

Hence, for the electrolytic cell for the aqueous solution of copper(II) bromide where graphite electrodes are used, the half-equations are:

$$2Br^-(aq) \rightarrow Br_2(l) + 2e^- \qquad E° = -1.09 \text{ V}$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E° = +0.34 \text{ V}$$

The electrons are balanced, and then the equations and $E°$ values are added together to determine the overall reaction and cell voltage for this electrolytic cell.

Overall reaction: $Cu^{2+}(aq) + 2Br^-(aq) \rightarrow Br_2(l) + Cu(s)$ $\quad E° = -0.75$ V

Therefore, more than 0.75 V must be supplied for this reaction to occur.

Consider a solution of copper(II) chloride, $CuCl_2$. The ions $Cu^{2+}(aq)$ and $Cl^-(aq)$ are present since it is a solution. Water is also present. Therefore, the possible reactions for both the anode and cathode reactions are determined.

- Oxidation occurs at the anode:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \qquad E° = -1.36 \text{ V}$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E° = -1.23 \text{ V}$$

- Reduction occurs at the cathode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E° = +0.34 \text{ V}$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83 \text{ V}$$

The preferred reactions are those with the least negative voltage at each electrode. Water will be oxidised at the anode and copper will be reduced at the cathode.

- Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E° = -1.23$ V
- Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E° = +0.34$ V

The electrons are balanced, and then the equations and $E°$ values are added together to determine the overall reaction and cell voltage for this electrolytic cell.

- Overall reaction: $2Cu^{2+}(aq) + 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 2Cu(s)$ $E° = -0.89$ V

Polyatomic anions, such as sulfate (SO_4^{2-}), nitrate (NO_3^-) and phosphate (PO_4^{3-}), are much more stable than monatomic anions. Hence, much larger voltages are required for them to be oxidised. Thus, when polyatomic anions are present in solution, the water will always be oxidised preferentially to the polyatomic anions, since it has a less negative voltage.

So, the overall reaction for the electrolysis of a copper(II) sulfate solution, $CuSO_4$, would be the same as the equation above:

- Overall reaction: $2Cu^{2+}(aq) + 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 2Cu(s)$ $E° = -0.89$ V

Concentration of electrolyte

In the electrolysis of aqueous solutions, there are competing reactions at both the anode and the cathode. The reaction at each electrode that has the lowest negative voltage – the reaction where the least voltage must be applied – is the favoured reaction. This is almost always true. However, where the $E°$ values for the competing reactions are very similar, the concentration of the solution may need to be considered.

Consider the previous example of copper(II) chloride, $CuCl_2$. At the cathode, there is a large difference between the $E°$ values for the reduction of copper(II) ions and the reduction of water. This indicates that the reduction of copper(II) ions is much more likely to occur than the reduction of water. Hence, concentration of the solution does not affect the preferred reaction for this electrode.

However, at the anode, there is only a very small difference between the $E°$ values for the oxidation of chloride and the oxidation of water. This indicates that there is very little difference in the likelihood of each of these reactions occurring. Hence, the concentration of the solution does affect the preferred reaction for this electrode. In a more concentrated solution, there are more chloride ions in the same volume of solution. Therefore, it is more likely that the chloride ions will be oxidised. However, in a more dilute solution, where there are fewer chloride ions in the same volume of solution, it is less likely that the chloride ions will be oxidised. The water will be oxidised in this case.

So, in more dilute chloride solutions, the anode reaction will be:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

while in more concentrated chloride solutions, the anode reaction will be:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

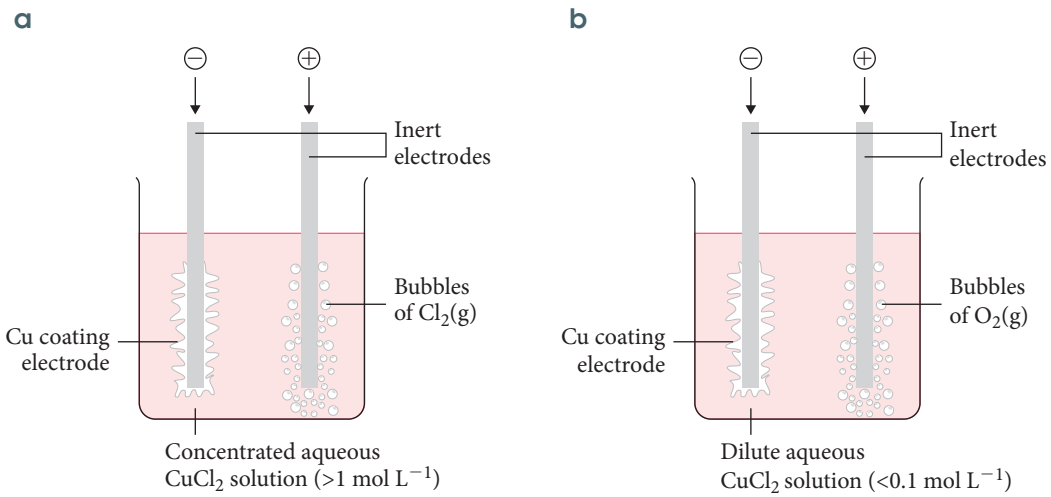


Figure C5.13 ▶ Electrolysis of copper(II) chloride under different conditions: a) concentrated aqueous solution and b) dilute aqueous solution

This is the most common example of where the concentration of the solution can affect the preferred reaction occurring at one of the electrodes. The other, less common, example is where zinc solutions are used.

- Cathode – reduction:

  $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $\quad E° = -0.76$ V

  $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad E° = -0.83$ V

Again, the $E°$ values are very close together which indicates that each of the reactions is equally likely to occur. Generally, the reduction of zinc ions would be the preferred reaction since it has the less negative $E°$ value; that is, less voltage must be applied for this reaction to occur. However, for very dilute zinc solutions, there would be very few zinc ions present in the solution. In this case, the reduction of water would occur.

Nature of the electrode

In each of the examples given for electrolysis so far, graphite electrodes have been used. Graphite electrodes are used in school experiments since they are good conductors of electricity, they are inert and relatively cheap. Platinum electrodes are generally used in industry because they are also inert and are good electrical conductors. Since both graphite and platinum are chemically inert under these conditions, they did not need to be considered in terms of anode and cathode reactions. However, if other more reactive electrodes are used, then they must also be considered when determining the preferred reactions at the anode and cathode.

Consider the copper(II) chloride cell again, but with copper electrodes instead of graphite electrodes. Once again, ions $Cu^{2+}(aq)$ and $Cl^-(aq)$ are present since it is a solution. Water is also present. However, Cu(s) is also present in the electrodes and could be oxidised. It must also be considered as a possible reaction at the anode. The method used is the same as the previous examples. However, one extra equation must be considered at the anode.

- Anode – oxidation:

  $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $\quad E° = -0.34$ V

  $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $\quad E° = -1.36$ V

  $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E° = -1.23$ V

- Cathode – reduction:

  $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E° = +0.34$ V

  $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad E° = -0.83$ V

The preferred reactions are those with the least negative voltage at each electrode. Copper will be oxidised at the anode and copper will be reduced at the cathode.

- Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $\quad E° = -0.34$ V
- Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E° = +0.34$ V

The electrons are balanced, and then the equations and E^0 values are added together to determine the overall reaction and cell voltage for this electrolytic cell.

- Overall reaction: $Cu^{2+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + Cu(s)$ $\quad E° = 0.00$ V

Therefore, if any voltage is applied to the cell, then the above reactions will occur. The anode will decrease in mass while the cathode will increase in mass.

This method is used industrially to purify copper. The final step in the extraction of copper from its ore to produce pure copper involves electrolysis. Blister copper, about 98 per cent pure copper from the smelting process, is the anode. A sample of pure copper is the cathode. The copper from the anode is oxidised and goes into solution. Pure copper, about 99.9 per cent, is deposited on the cathode. The impurities either stay in solution or fall to the bottom of the electrolytic cell.

Electrolysis can also be used for electroplating one metal onto another. Silver plating cutlery and jewellery are common examples of electroplating. The metallic object that is to be plated is the cathode in the electrolytic cell. The electrolyte is a solution containing the metal to be plated on the object. The anode is either an inert electrode or the metal to be plated on the object – this is dependent on the reactivity of the metal. In this example, the jewellery would be the cathode. A solution of silver nitrate would be the electrolyte and a silver anode would be used. The silver at the anode would be oxidised to form silver ions. The silver ions would move to the cathode where they will undergo reduction and form a silver deposit on the jewellery.

EXPERIMENT 5.3

ELECTROPLATING

Electroplating is an important industrial process. Here, the students can model the process.

Aim

To silver plate a piece of copper using electrolysis

Materials

- 20 mL of a saturated potassium iodide solution, KI
- 30 mL of a 0.1 mol/L silver nitrate solution, $AgNO_3$
- Stirring rod
- Sandpaper
- Warm solution of detergent
- 100 mL beaker
- 1 graphite electrode
- 1 strip of copper
- Powerpack
- 2 electrical leads with banana plugs
- 2 alligator clips, one to be placed on each electrical wire
- Waste bottle for heavy metals

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Silver nitrate stains skin.	Rinse the piece of copper under water before touching it.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. While stirring, add the saturated potassium nitrate to 30 mL of the silver nitrate solution until the precipitate that forms is dissolved.
2. Clean the piece of copper using sandpaper, then wash in a warm solution of detergent and rinse thoroughly.
3. Attach the piece of copper to the negative terminal and the graphite electrode to the positive terminal of the powerpack.
4. Set the powerpack to 4 V and turn it on.
5. Record observations.
6. Dispose of the copper(II) sulfate by pouring it into the heavy metals waste bottle. Do not pour it down the drain.

Results

Record all of your observations.

Analysis

1. Identify the anode in this electrolytic cell.
2. Identify the cathode in this electrolytic cell.
3. Write the half equation for the reaction occurring at the anode.
4. Write the half equation for the reaction occurring at the cathode.

Discussion

1. Write the overall equation for the electroplating reaction.
2. Justify why the metal to be electroplated onto the object is sometimes used as the anode instead of an inert electrode such as graphite.
3. Explain why electroplating is used instead of using pure metal. For example, why would a jeweller use silver plating instead of pure silver?
4. Relate your experimental method to the industrial use of electrolysis in electroplating.

INVESTIGATION 5.1

FACTORS THAT AFFECT ELECTROLYSIS

We have looked at three factors that affect the nature of the reactions at each of the electrodes in an electrolytic cell:

- nature of the electrolyte
- concentration of the electrolyte
- nature of the electrode.

You will choose one of these factors and plan and perform an investigation to verify the effect of your identified factor on the reactions at the anode and cathode in an electrolytic cell.

What is your aim?

Which of the above factors will you investigate?

What will you need?

1 What chemicals will you need and how much of them will you need?

2 What equipment will you need?

What are the risks?

Complete the risk assessment box to show any risks associated with completing this investigation and ways to manage them.

What are the risks in doing this investigation?	How can you manage these risks to stay safe?

How will you carry out your investigation?

1 How will you ensure that your investigation is valid and reliable?

2 How will you be able to verify the reactions that are occurring at each of the electrodes?

3 Write a procedure to clearly indicate your method.

4 A diagram of your experimental set up may assist with demonstrating your understanding.

What results will you collect?

1 What data will you collect?

2 Clearly present all of your results in an appropriate format.

How will you analyse your results?

What data will you need to compare to determine if your results support your aim?

What have you found?

Did your results show any differences in the reactions at the anode and the cathode when you changed your independent variable?

What do you conclude?

1 Do your results answer your aim?

2 Are your results consistent with the theory? Support your statement with evidence from your investigation.

Ideas for improvement or further investigation

1 Was your investigation valid and reliable? If not, suggest ways in which the method should be modified.

2 Could you have improved the accuracy of your results? If so, how could you achieve this?

INVESTIGATION 5.2

FACTORS THAT AFFECT THE RATE OF AN ELECTROLYSIS REACTION

The rate of a chemical reaction is the speed at which a chemical reaction occurs – quickly or slowly. You learnt about this in *Nelson Chemistry Units 1 & 2 for the Australian Curriculum*, Chapter 9. Some factors that may affect the rate at which an electrolysis reaction occurs are the:

- applied voltage
- surface area of the electrodes
- concentration of the electrolyte
- distance between the electrodes.

Choose one of these factors and plan and perform an investigation to determine the effect of your identified factor on the rate of your electrolysis reaction.

What is your aim?

Which of the above factors will you investigate?

What will you need?

1 What chemicals will you need and how much of them will you need?

2 What equipment will you need?

What are the risks?

Complete the risk assessment box to show any risks associated with completing this investigation and ways to manage them.

What are the risks in doing this investigation?	How can you manage these risks to stay safe?

How will you carry out your investigation?

1 How will you ensure that your investigation is valid and reliable?

2 How will you be able to measure or determine the rate at which the reaction is occurring?

3 Write a procedure to clearly indicate your method.

4 A diagram of your experimental set-up may assist with demonstrating your understanding.

What results will you collect?

1 What data will you collect?

2 Clearly present all of your results in an appropriate format.

How will you analyse your results?

What data will you need to compare to determine if your results support your aim?

What have you found?

Did your results show any difference in the rate of the electrolysis reaction when you changed your independent variable?

What do you conclude?

1 Do your results answer your aim?

2 Use your knowledge of factors that affect the rate of a chemical reaction and apply this to the factor you were investigating to explain your results. Support your statements with evidence from your investigation.

Ideas for improvement or further investigation

1 Was your investigation valid and reliable? If not, suggest ways in which the method should be modified.

2 Could you have improved the accuracy of your results? If so, how could you achieve this?

QUESTION SET 5.4

Remembering

1 Identify the energy transformation that takes place in an electrolysis reaction.

2 Identify the factors that affect the chemistry of the electrolysis of an aqueous salt.

3 Identify the type of reaction that occurs at the anode of an electrolytic cell.

Understanding

4 Why is the chemistry of the electrolysis of a molten salt easier to understand than the chemistry of an aqueous salt?

5 Draw a labelled diagram to show the set-up of an electrolytic cell.

Applying

6 A student set up an electrolysis experiment to decompose a sample of molten zinc bromide using graphite electrodes.

- **a** Identify any risks associated with this investigation and describe how these risks could be minimised.
- **b** Identify the anode reaction, cathode reaction and cell voltage for this electrolytic cell.

7 A student set up an electrolysis experiment using a dilute solution of aqueous iron(II) iodide and inert electrodes.

- **a** Identify the anode reaction.
- **b** Identify the cathode reaction.
- **c** Outline the observations for each electrode.
- **d** Determine the voltage that would need to be applied to operate this electrolytic cell.

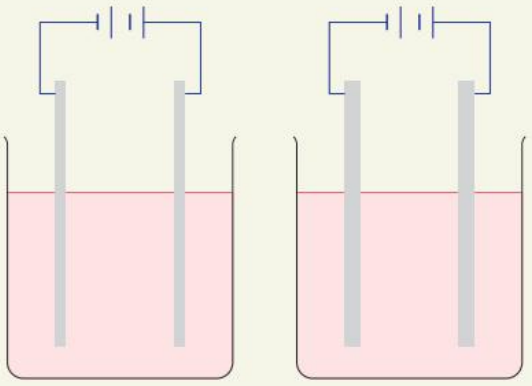
8 A student set up an electrolysis experiment using a dilute solution of aqueous calcium chloride and inert graphite electrodes.

- **a** Identify the anode reaction.
- **b** Identify the cathode reaction.
- **c** Outline the observations for each electrode.
- **d** How could you identify the products forming at each electrode?
- **e** Determine the voltage that would need to be applied to operate this electrolytic cell.

Analysing

9 A student set up the electrolysis experiments in Figure C5.14 to determine the effect of the spacing of electrodes on the rate of an electrolysis reaction.

Justify why their results would be invalid and explain how they could modify their investigation to ensure that their results were valid.



▲ **Figure C5.14** Experimental set-up

CHAPTER CHECKLIST

You should know:

- electrochemical cells involve the transformation of energy between chemical potential energy and electrical energy
- there are two types of electrochemical reactions: galvanic cells and electrolytic cells
- standard electrode potentials are the voltages of the test cell relative to the standard hydrogen cell
- the conditions under which the table of standard electrode potentials are determined:
  - Solutions must contain 1 mol L^{-1} of ions of the species being tested.
  - Solutions must be at 25°C.
  - Gases must be at 100 kPa and 25°C.
- galvanic cells convert chemical potential energy to electrical energy
- galvanic cells are spontaneous electrochemical reactions and have a positive overall voltage
- galvanic cells require an anode, a cathode, an external circuit and a salt bridge
- galvanic cells contain a voltmeter
- inert electrodes such as graphite or platinum are used when the half-cell:
  - involves a mixture of solutions of a metal with varying oxidation states
  - involves a gas being bubbled in and a solution containing ions of that gas
- fuel cells are an example of a galvanic cell
- fuel cells involve a fuel and an oxidant and convert chemical energy directly to electrical energy without the need for any combustion reactions
- the most common fuel used in a fuel cell is hydrogen
- fuel cells vary in the type of electrolyte used
- catalysts improve the efficiency of fuel cells
- platinum is the most common catalyst used in fuel cells
- metal nanoparticles are being used as catalysts to improve the efficiency and decrease the cost of fuel cells
- electrolytic cells convert electrical energy into chemical potential energy
- electrolytic cells are not spontaneous electrochemical cells; they have a negative overall voltage
- electrolytic cells contain a source of electricity, such as a powerpack or battery
- electrolysis of aqueous solutions involves competing reactions at both the anode and the cathode
- the factors that affect the possible reactions at the anode and the cathode are the nature and concentration of the electrolyte and the nature of the electrode
- electrolytic cells are used in industry; for example, purification of copper and electroplating.

You should be able to:

- draw a diagram to show the set-up for experimentally determining the standard cell potentials
- use a table of standard electrode potentials to determine the relative oxidation or reduction strength of species
- draw a diagram to represent a galvanic cell, including anode, cathode, salt bridge and direction of electron flow through the external circuit
- use a table of standard electrode potentials to determine half-equations for anode and cathode reactions
- calculate the cell voltage for a galvanic cell, using a table of standard electrode potentials
- construct galvanic cells from different metals and electrolytes
- use a table of standard electrode potentials to determine the competing reactions at both the anode and the cathode in electrolytic cells
- determine which of the competing reactions is the preferred reaction at each electrode in electrolytic cells
- calculate the cell voltage for an electrolytic cell
- construct an electrolytic cell
- identify independent and dependent variables
- plan a valid and reliable investigation.

CHAPTER GLOSSARY

anode the electrode where reduction occurs

cathode the electrode where oxidation occurs

electrochemical cell a cell that transforms energy between electrical energy and chemical potential energy

electrolyte a solution that conducts an electric current

electrolytic cell a type of electrochemical cell that transforms electrical energy to chemical potential energy; this is not a spontaneous reaction, it requires the input of electrical energy for the chemical reaction to occur

fuel cell a galvanic cell that occurs where a fuel, such as hydrogen or methanol, is oxidised and oxygen is reduced releasing electrical energy

galvanic cell a type of electrochemical cell that transforms chemical potential energy to electrical energy in a spontaneous chemical reaction

salt bridge allows the movement of ions to complete the circuit in a galvanic cell

CHAPTER REVIEW QUESTIONS

Remembering

1 Each of the following statements is false. Correct the statements so that they are true.
   - a The anode is the site of oxidation in a galvanic cell but is the site of reduction in an electrolytic cell.
   - b A fuel cell gets hot when it is operating since it converts chemical energy to heat energy.

2 Identify the energy transformation in an electrolytic cell.

3 Identify the role of platinum in a fuel cell.

4 Identify two factors that affect the rate of an electrolysis reaction.

Understanding

5 Explain why a battery or powerpack is used in an electrolytic cell.

Applying

6 Identify the anode reaction, cathode reaction, cell voltage and direction of electron flow for each of the following galvanic cells.
   - a Lead, lead(II) ion electrode connected with a salt bridge to an aluminium, aluminium ion electrode.
   - b An electrode containing platinum in a mixture of bromine and bromide solution connected with a salt bridge to another piece of platinum in a mixture of solutions of tin(II) and tin(IV).

7 Use cell notation to represent each of the galvanic cells in Question 6.

8 A piece of zinc was put in a beaker of zinc sulfate solution. A salt bridge connected this beaker to another beaker that contained an acidified potassium permanganate solution, $KMnO_4$. The zinc electrode and the electrode in the other beaker were connected to a voltmeter.
   - a Draw a diagram to show this galvanic cell.
   - b Identify the electrode in the second beaker.
   - c Identify the anode and cathode reactions for this galvanic cell.
   - d Calculate the cell voltage and the direction of electron flow through the external circuit.

9 A student poured some iron(II) nitrate and copper(II) nitrate into a beaker. They placed graphite electrodes in the beaker and connected them to a powerpack.
   - a Identify the anode reaction.
   - b Identify the cathode reaction.
   - c Write an overall equation for this electrolytic cell and calculate the cell voltage.

Analysing

10 Justify why sodium can only be extracted from a molten salt not an aqueous solution of a salt.

11 Justify whether this reaction will occur spontaneously:
$Zn(s) + Mn^{2+}(aq) \rightarrow Mn(s) + Zn^{2+}(aq)$

Evaluating

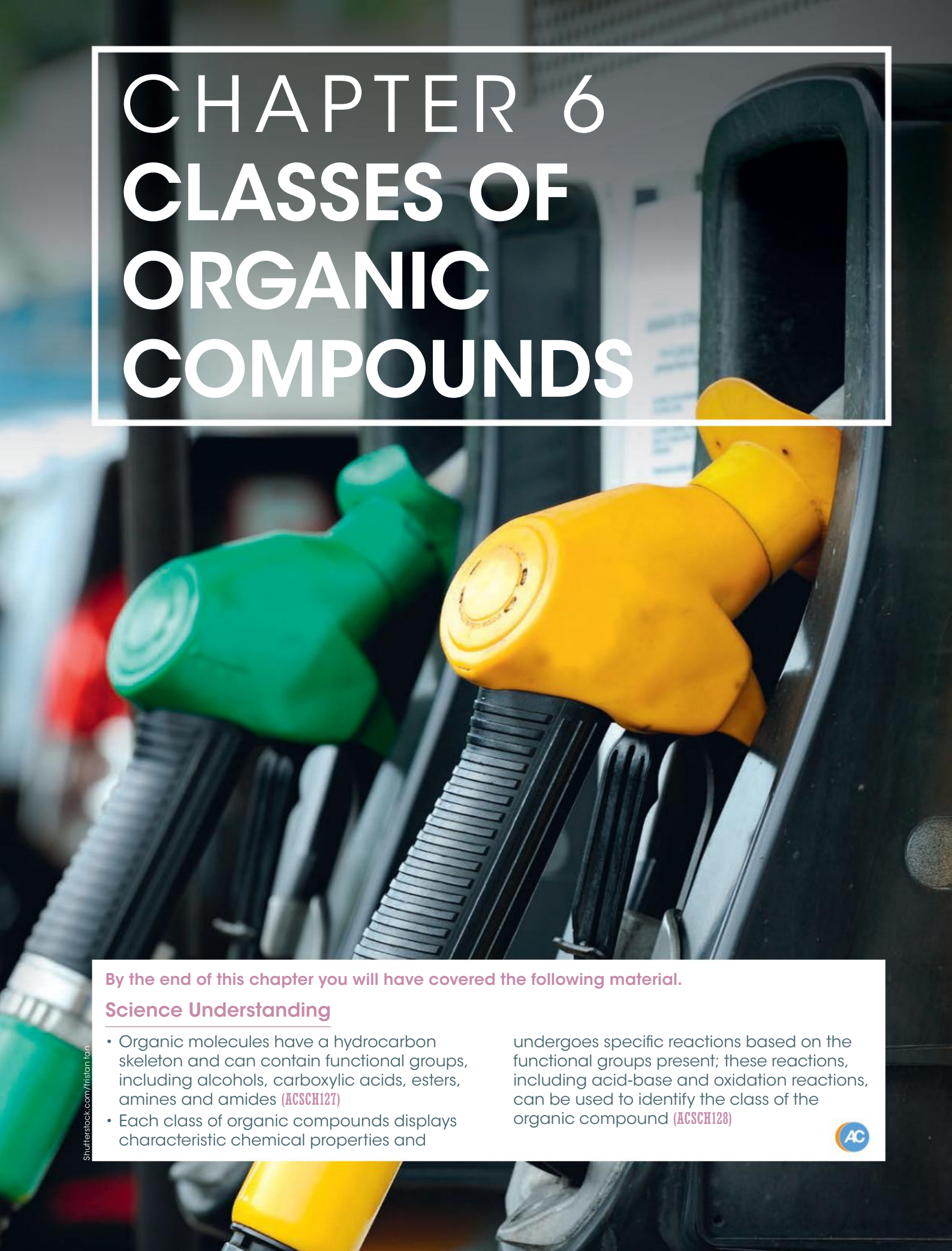
12 A student set up a galvanic cell. One electrode consisted of a beaker containing a piece of magnesium in a solution containing 0.5 mol L^{-1} magnesium sulfate. The other electrode consisted of a beaker where chlorine gas was bubbled into a solution containing 0.5 mol L^{-1} sodium chloride. A piece of filter paper soaked in silver nitrate was used to connect the beakers. A voltmeter was placed in the external circuit. Evaluate whether this cell will function effectively. Give reasons for your answer.

Reflecting

13 Develop a PMI chart on electrochemistry.

14 Why are electrolytic cells set up in a single container rather than the two containers used for galvanic cells?

CHAPTER 6
CLASSES OF ORGANIC COMPOUNDS



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By the end of this chapter you will have covered the following material.

Science Understanding

- Organic molecules have a hydrocarbon skeleton and can contain functional groups, including alcohols, carboxylic acids, esters, amines and amides (ACSCH127)
- Each class of organic compounds displays characteristic chemical properties and undergoes specific reactions based on the functional groups present; these reactions, including acid-base and oxidation reactions, can be used to identify the class of the organic compound (ACSCH128)

6.1 Organic families



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Figure C6.1 ▲ An organic chemist at work

Chemists in the 17th and 18th centuries knew that chemicals such as sugars, carbohydrates, fats, oils and proteins, which were obtained from living things, were different from the chemicals obtained from rocks. The term **organic compound** was used to describe substances obtained from living things while the term **inorganic compound** described any substance not obtained from an animal or plant source.

Early chemists believed that only organic chemicals could be used to make other organic chemicals. Ideas changed quickly when the German chemist Friedrich Wohler synthesised the typical 'organic' compound, urea, from a typical 'inorganic' compound. As more organic compounds were made from inorganic sources, it became clear that compounds found in living things and those obtained from non-living sources such as rocks and minerals were part of the same chemical system.

The study of organic compounds is the branch of chemistry called organic chemistry, also known as carbon chemistry.

Organic molecules are built on a skeleton of covalently bonded carbon atoms.

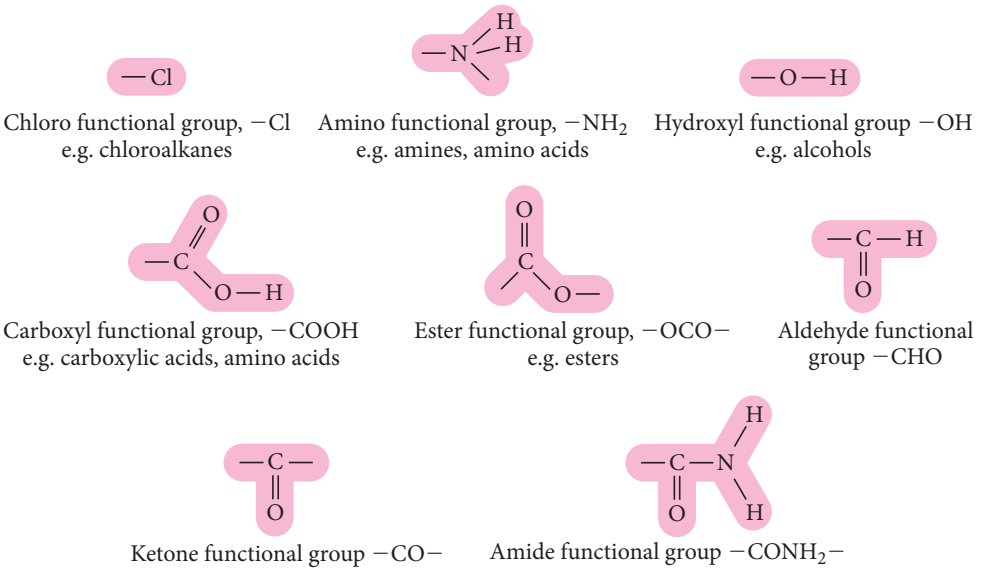
There are millions of natural and synthetic organic compounds and every day new ones are being synthesised or isolated. More than 90 per cent of all known compounds are organic. Because there are so many organic compounds, chemists have developed and use a classification system based on the structural features of compounds because the three-dimensional structure of a molecule determines its chemical identity. The types of atoms present in a molecule and the way in which they are arranged determines the physical and chemical properties of the molecule.

The types of atoms present in a molecule and the overall shape in which they are arranged determine in which chemical interactions and reactions the molecule can participate.

Compounds are grouped into series of 'families' of related compounds, which share key chemical properties. Most commonly, these properties arise from the presence of one or more particular groups of atoms, called **functional groups**.

This classification system is extremely useful because knowing the properties and reactivities of one member of a family allows you to predict the properties and reactivities of other

Figure C6.2 ▶ The functional groups present in some important organic families



family members. Similarly, finding ways to modify one member in a particular way provides information on how to modify another member in the same way.

Organic chemicals can be classified into groups or 'families' of related compounds that share key chemical characteristics.

Bonding in carbon

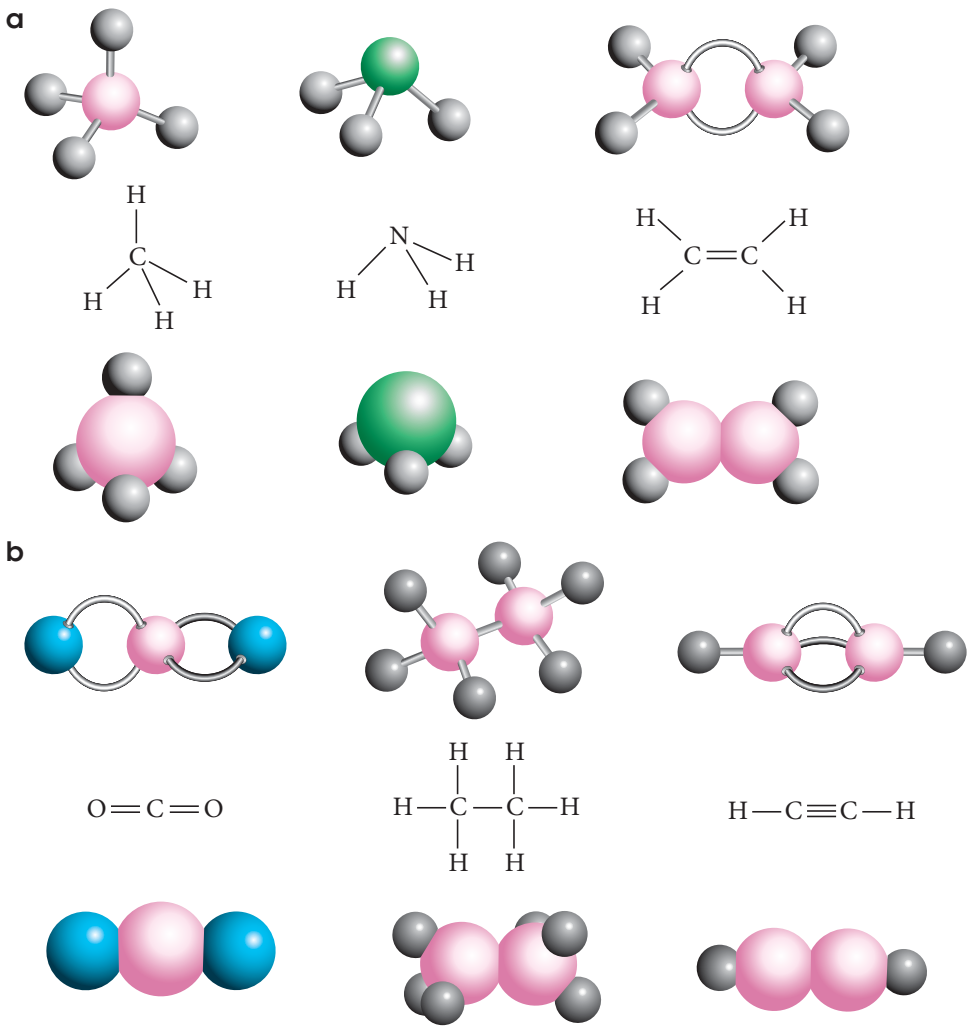
In organic compounds, carbon atoms almost always form four bonds. For this to occur, the four valence electrons must be involved in the bonding. In simple carbon-based compounds such as alkanes, there are four identical bonds and a tetrahedral orientation of the electron pairs with an angle of 109.5° between bonds.

One, two or three pairs of the valence electron from adjoining carbon atoms may be involved in the bonding to form:

- single bonds (one shared pair of electrons) C—C
- double bonds (two shared pairs of electrons) C═C
- triple bonds (three shared pairs of electrons) C≡C.

Valence electrons not involved in forming carbon–carbon bonds form bonds with other elements, typically hydrogen, oxygen and nitrogen.

The physical appearance of molecules can be visualised by space-filling models. However, these models do not show the nature of the chemical bonding very clearly so chemists use ball and stick models in which the atoms are represented by balls and the bonds by sticks. Figure C6.3 shows a comparison of these two models with their structural formula.



◀ **Figure C6.3**
Ball and stick models, structural formulas and space-filling models of (left to right): a) methane, ammonia and ethene; and b) carbon dioxide, ethane and ethyne

Table C6.1 provides a summary of the geometrical arrangement of bonds around carbon atoms.

Table C6.1 Geometrical arrangement of bonds around carbon atoms

Bonds around the C atom		Geometrical arrangements of the bonds	Example
Four single bonds		Tetrahedral	Methane
One double and two single		Planar (angle between bonds 120°)	Ethene
Two double bonds		Linear	Carbon dioxide
One triple and one single		Linear	Ethyne

QUESTION SET 6.1

Remembering

1 Write the ground state electron configuration for a neutral carbon atom.
2 Describe the difference between an organic compound and an inorganic compound.
3 Explain why carbon with four single bonds forms a tetrahedral structure.

Understanding

4 Draw the electron dot diagram for:
   a C_2H_6
   b CH_3Cl
   c C_2H_4
5 Draw the structural formula for each of the molecules in Question 4.

6.2 Hydrocarbons

Key:  is the symbol for the benzene ring shown below. The ring represents a ring of shared electrons.

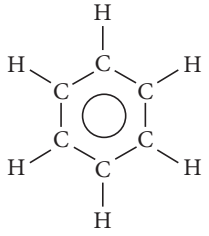


Figure C6.4 ▲ Benzene

In *Nelson Chemistry Units 1 & 2 for the Australian Curriculum*, you learnt that hydrocarbons are compounds made up of only hydrogen and carbon. Almost all other organic compounds can be considered to be derivatives of simple hydrocarbons. Hydrocarbons can be classified as aliphatic or aromatic.

Aromatic hydrocarbons contain one or more benzene rings; these molecules will be considered in more detail later in this chapter. Figure C6.4 shows the structure of a benzene ring.

Aliphatic compounds are all other hydrocarbons. The carbon atoms may be bonded in chains or non-aromatic rings. The chain compounds may be further classified into families on the basis of individual carbon–carbon bonds.

The family of chain hydrocarbon compounds where all the carbon–carbon bonds are single bonds is called **alkanes**. Compounds with only single bonds between carbon atoms are called **saturated compounds**.

The family of chain hydrocarbon compounds in which at least one of the carbon–carbon bonds is a double bond is called **alkenes**. Compounds with at least one multiple bond (double or triple) between carbon atoms are called **unsaturated compounds**.

The hydrocarbon families of alkanes and alkenes were considered in *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 3.

WOW

Saturated and unsaturated

The terms 'saturated' and 'unsaturated' originated before chemists understood the structure of organic compounds. They knew that some hydrocarbons would react with hydrogen in the presence of a catalyst while other hydrocarbons would not. When a substance would not react with any more hydrogen, it was considered to be 'saturated' with hydrogen while hydrocarbons that would react with more hydrogen were referred to as 'unsaturated'.

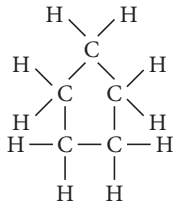
There are two other families of aliphatic hydrocarbons – alkynes and alicyclic compounds.

Alkynes are the family of chain hydrocarbons that have at least one carbon–carbon triple bond. Like alkenes, alkynes are classified as unsaturated compounds.

Hydrocarbon compounds in which the carbon atoms have joined to form a closed ring structure are called **alicyclic**, or more commonly, cyclic hydrocarbons. Cyclic hydrocarbons containing from as few as three to as many as 30 carbon atoms have been identified. Five- and six-membered rings are most common in nature.

Cyclic hydrocarbons may be saturated or unsaturated. Those that contain only C—C single bonds are **cycloalkanes**, those with C=C double bonds are **cycloalkenes** and those with C≡C triple bonds are **cycloalkynes**. Cyclic compounds are named by adding the prefix 'cyclo-' to the name of the corresponding aliphatic hydrocarbon. Figure C6.5 shows examples of each of these cyclic hydrocarbon groups.

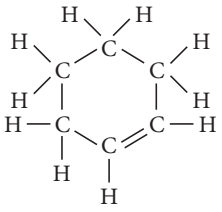
Although the structures are different, cyclic hydrocarbons have similar physical and chemical properties to the corresponding chain aliphatic hydrocarbon. They will not be considered in more detail in this text.



Cyclopentane



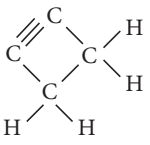
Cyclopentane simplified structural formula



Cyclohexene



Cyclohexene simplified structural formula



Cyclobutyne



Cyclobutyne simplified structural formula

◀ **Figure C6.5**
Examples of cyclic hydrocarbons showing the structural formulas

WOW

Pyrethrins

Cyclopropane rings are not often found naturally because they are not very stable. One exception is the group of compounds known as pyrethrins found in chrysanthemums. These compounds act as natural insecticides that protect the leaves from insect predators. Pyrethrins extracted from their natural source are used in many pest control formulas, including insecticide sprays, and flea and tick control products.

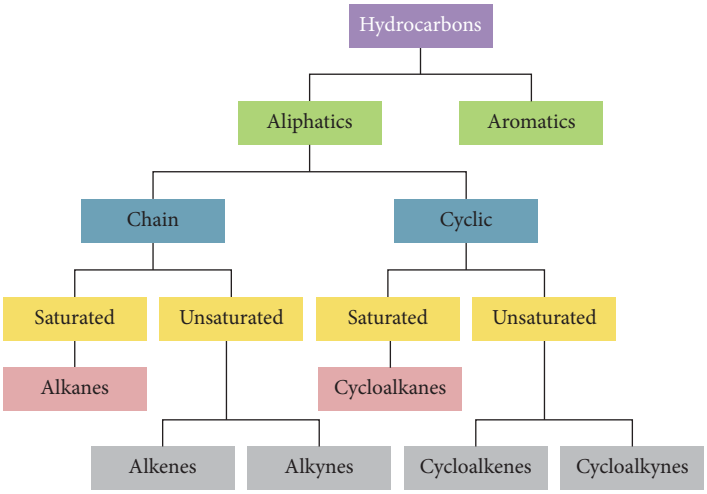


Lyudmila Suvorova/Shutterstock.com

Figure C6.6 ▶
Chrysanthemum cinerariifolium is a source of pyrethrin – a cyclopropane compound.

Figure C6.7 summarises the main groups of hydrocarbons.

Figure C6.7 ▶
Groups of hydrocarbons



Structure and bonding

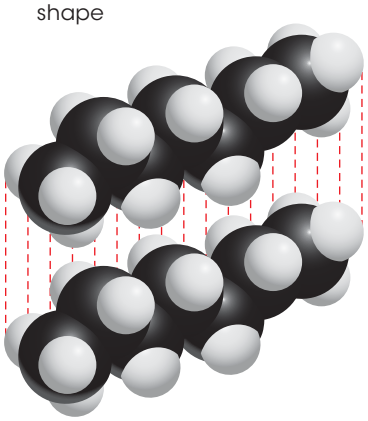
Hydrocarbons are classified as **non-polar** molecules. This is due to carbon and hydrogen having similar electronegativity and the relatively symmetrical shape of most hydrocarbon molecules. As a result the only intermolecular force of attraction between adjacent molecules is **dispersion forces**.

The strength of the dispersion forces between hydrocarbon molecules increases when the molecules are:

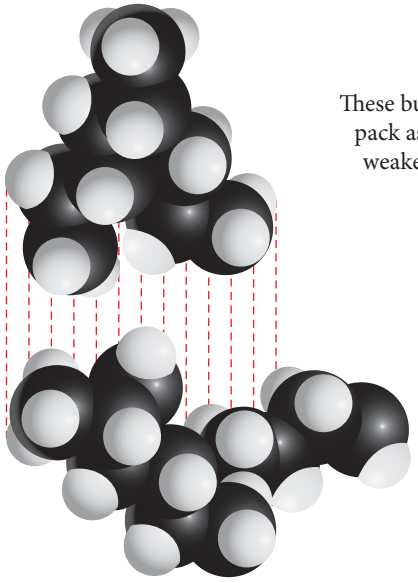
- closer together (this depends on molecular shape)
- larger as there are more regions of charge to attract each other.

Figure C6.8 shows how these factors affect the strength of dispersion forces between molecules.

Figure C6.8 ▶
Factors that affect attraction between hydrocarbon molecules: size and shape



Key: - - - - - - - dispersion forces



These bulky molecules cannot pack as closely and so have weaker dispersion forces.

Properties of alkanes and alkenes

To revise alkanes and alkenes, refer to Nelson Chemistry Units 1 & 2, *Chapter 3*

Table C6.2 summarises many of the properties of alkanes and alkenes discussed in *Nelson Chemistry Units 1 & 2 for the Australian Curriculum*. The majority of these properties are also similar for alkynes and corresponding cyclic compounds.

Table C6.2 Properties of alkanes and alkenes

Property	Alkane	Alkene
Electrical conductivity	Non-conducting due to non-polar molecules	Non-conducting due to non-polar molecules
Melting point and boiling point	Small molecules have low melting and boiling points because of weak dispersion forces between molecules. Melting and boiling point increases with molecular size	Small molecules have low melting and boiling points because of weak dispersion forces between molecules. Melting and boiling point increases with molecular size
Solubility	Insoluble in polar solvents Soluble in non-polar solvents	Insoluble in polar solvents Soluble in non-polar solvents
Combustion reaction (oxidation—reduction reaction)	Flammable (smaller molecules are highly flammable) React with oxygen to produce carbon dioxide and water For example: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$	Flammable (smaller molecules are highly flammable) React with oxygen to produce carbon dioxide and water For example: $C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(g)$
Substitution reaction	Undergo substitution reactions in the presence of ultraviolet (UV) light or at high temperatures. Chlorine or bromine replace H atoms. For example: $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$ $C_6H_{14}(g) + Br_2(soln) \rightarrow C_6H_{13}Br(soln) + HBr(soln)$	Usually do not undergo substitution reactions.
Addition reaction	Do not undergo addition reactions because no multiple bond present	Undergo a large number of addition reactions involving the breaking of the double bond and bonding new species to carbon **a** React with hydrogen (hydrogenation) in the presence of a catalyst to produce an alkane. For example: $CH_2{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_3(g)$ **b** React with a halogen (halogenation) to produce a haloalkane. For example: $CH_3{-}CH{=}CH_2(g) + Cl_2(g) \rightarrow CH_3CHCl{-}CH_2Cl(g)$ **c** React with water in the presence of an acid to produce an alcohol. For example: $CH_2{=}CH_2(g) + H_2O(g) \rightarrow CH_3{-}CH_2OH(l)$

Isomers of alkenes

In *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 3 you learnt that compounds that have the same molecular formula but different structural formula are called **isomers**. Figure C6.9 shows the two isomers of butene, 1-butene and 2-butene.

A closer look at 2-butene shows that it has two structures (Figure C6.10).

Figure C6.9 ▶ The structural isomers of butene

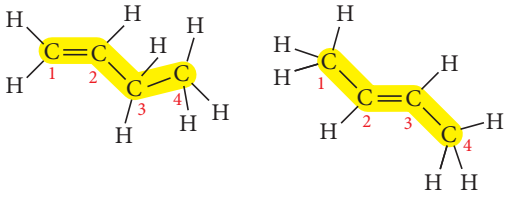
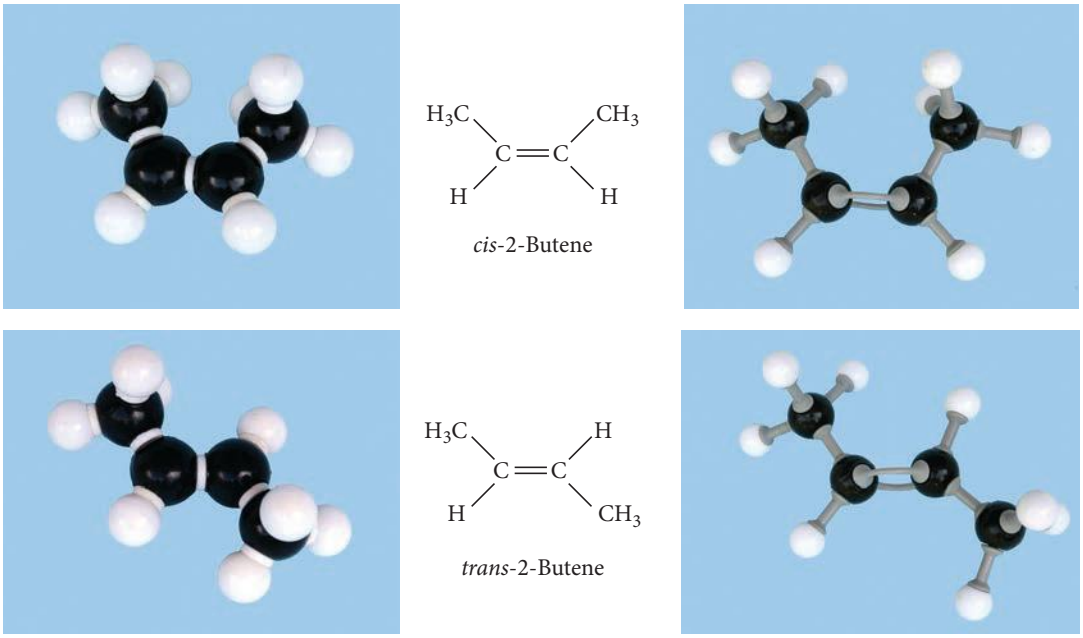


Figure C6.10 ▶ Space-filling, structural and ball and stick models of *cis*- and *trans*-2-butene



The geometry around the double bond is planar with all the bond angles being 120°. Carbon atoms on either side of the double bond cannot rotate around the bond. The isomerism resulting from the presence of a double bond is **geometrical** or ***cis–trans*** isomerism. The word *cis* means the same side while *trans* means opposite sides. Geometrical isomerism is possible whenever each carbon on the double bond has at least one branch.

In the first structure in Figure C6.10, both the methyl groups are on the same side of the double bond so this compound is named *cis*-2-butene. In the second structure, they are on opposite sides so it is named *trans*-2-butene. These two structures represent distinct compounds with different melting points, boiling points and densities as shown in Table C6.3.

Table C6.3 Different properties of *cis*- and *trans*-2-butene

Compound	Melting point (°C)	Boiling point (°C)	Density ($g\,mL^{-1}$)
cis-2-Butene	−139	4	0.615
trans-2-Butene	−105.6	1	0.598

To see how this affects the properties of rubber, refer to Context 4, 'Polymer chemistry', page 91.

Geometric isomers are compounds that differ only in the geometrical arrangement of the same groups of atoms in the molecule and therefore have different physical properties.

WOW

Pheromones

Pheromones are organic compounds produced by an organism to communicate with other members of its species. Some pheromones are used for sexual attraction, some to mark territories or trails and others to warn of danger. Pheromones have been used extensively in agriculture in insect traps. Many pheromones are long-chain alkenes containing a small number of functional groups. Reactions involving pheromones are isomer specific and sometimes it is only one isomer – the *cis* or *trans* – that is biologically active.



Fritz Geller-Grimm/Wikimedia Commons/CC-BY-SA-2.5

▲ **Figure C6.11** An insect pheromone trap

Uses of alkanes and alkenes

The main use of alkanes is fuels.

- Methane is the main component of natural gas.
- Propane is also known as LPG (liquid petroleum gas).
- Octane is the main constituent of automobile gas.
- Pentane is used as a solvent.
- Nonane and decane are both used in petrol.

The longer chain molecules are fuel oil and mineral oils and are used as lubricants. Other heavier molecules (C_{16} to C_{24}) are the basis of petroleum jelly, greases, paraffin wax and asphalt.

The low molecular mass alkanes are the starting materials for many organic chemistry based industries, such as paint and plastic manufacture.

The main use of alkenes is as the basis of the petrochemical industry – especially those with low molecular mass. They are used as starting materials in the syntheses of alcohols, plastics, lacquers, detergents and fuels.

Ethene is the most important organic feedstock in the chemical industry. Ethene is produced from natural gas and crude oil by cracking. It is used as feedstock for many chemical products such as polyethylene, vinyl chloride, styrene, ethanol, acetaldehyde and many more. It is also used for artificial ripening of fruits, as a general anaesthetic, and to generate an ethylene-oxygen flame.

Propene, the second most important feedstock for organic products, is mainly used for the production of polypropylene and various oxidation products such as butanol, acrylic acid, acrolein, acrylic acid ester, glycerol, allyl chloride and epichlorohydrin.

Alkynes

Alkynes are a family of hydrocarbons containing at least one triple bond between a pair of carbon atoms (C≡C). The alkynes, like the alkenes, are unsaturated hydrocarbons.

The simplest member ethyne, C_2H_2, is a linear molecule as shown in Figure C6.3 (page 281). Ethyne is commonly called acetylene and is widely used in oxyacetylene torches for cutting and welding.

The names and formulas of the first nine alkynes is given in Table C6.4.



SantiPhotoSS/Shutterstock.com

▲ **Figure C6.12** Oxyacetylene torches are widely used for cutting and welding steel.

Table C6.4 Names and formula of the first nine alkynes

Name	Formula
Ethyne	C_2H_2
Propyne	C_3H_4
Butyne	C_4H_6
Pentyne	C_5H_8
Hexyne	C_6H_{10}
Heptyne	C_7H_{12}
Octyne	C_8H_{14}
Nonyne	C_9H_{16}
Decyne	$C_{10}H_{18}$

From Table C6.4, it can be seen that alkynes have the general formula C_nH_{2n-2}. As with alkanes, each successive member of the series is formed by adding CH_2 to the formula of the previous member.

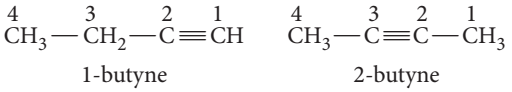
Naming alkynes

As with alkenes, isomerism is possible in straight-chain alkynes with four or more carbon atoms. The location of the triple bond needs to be included in the name.

To name straight-chain alkynes:

1. to the usual stem name (for example, eth-, but-), which indicates the number of carbon atoms in the chain, add the ending '-yne'
2. determine the location of the triple bond by numbering the carbon atoms from the end of the chain closest to the triple bond
3. show the location of the triple bond by putting in front of the name the number of the carbon at which the triple bond starts followed by a hyphen. (Numbers are not used for ethyne and propyne because they have no isomers.)

The first compound shown below is 1-butyne whereas the second is 2-butyne:



1-butyne 2-butyne

Properties of alkynes

As might be expected, the physical properties of alkynes are similar to those of alkanes and alkenes. As a family, they show similar trends in melting point, boiling point and state under normal conditions. Alkynes are non-polar so are sparingly soluble in polar solvents such as water but are soluble in non-polar solvents. These properties are due to the weak dispersion forces between molecules.

Chemical reactivity

Combustion reactions

Like alkanes and alkenes, alkynes undergo combustion in a plentiful supply of oxygen to produce carbon dioxide and water.

For example:

$$C_3H_4(g) + 4O_2(g) \rightarrow 3CO_2(g) + 2H_2O(g)$$

Addition reactions

Alkynes also undergo addition reactions but they are less reactive than alkenes. The addition reaction usually takes place in two steps. In the first step, addition of a reagent results in the triple bond being converted to a double bond, then in a second addition step the double bond is broken, resulting in a saturated compound.

a **Hydrogenation:** Alkynes react with hydrogen gas (hydrogenation). Under pressure, hydrogen adds to an alkyne in the presence of a metal catalyst such as finely divided nickel, palladium or platinum to form a corresponding alkene or alkane.

For example:

$$\underset{\text{Ethyne}}{CH{\equiv}CH(g)} + \underset{\text{Hydrogen}}{H_2(g)} \rightarrow \underset{\text{Ethene}}{CH_2{=}CH_2(g)} \text{ (Pd catalyst and inhibitor)}$$

or

$$\underset{\text{Ethyne}}{CH{\equiv}CH(g)} + 2\underset{\text{Hydrogen}}{H_2(g)} \rightarrow \underset{\text{Ethane}}{CH_3{-}CH_3(g)} \text{ (Pd catalyst)}$$

If an inhibitor is added, its presence prevents ethene from being hydrogenated to the saturated alkane.

b **Halogenation:** Alkynes react with a halogen (halogenation). For example, when bromine or chlorine are added across the triple bond, a substituted haloalkene is formed. A second step then produces a haloalkane.

For example:

$$\underset{\text{Ethyne}}{CH{\equiv}CH(g)} + \underset{\text{Bromine}}{Br_2(aq)} \rightarrow \underset{\text{1,2-Dibromoethene}}{CHBr{=}CHBr(aq)}$$

$$\underset{\text{1,2-Dibromoethene}}{CHBr{=}CHBr(g)} + \underset{\text{Bromine}}{Br_2(aq)} \rightarrow \underset{\text{1,1,2,2-Tetrabromoethane}}{CHBr_2{-}CHBr_2(aq)}$$

EXPERIMENT 6.1

COMPARING REACTIVITIES OF ALKANES AND ALKENES (TEACHER DEMONSTRATION)

The reactivities of alkanes and alkenes are different. Alkanes react quite slowly by a process of substitution while alkenes react rapidly, usually by the process of addition.

Aim

To compare the reactivities of alkanes and alkenes

Materials

- 3 mL samples of alkanes and alkenes: hexane, cyclohexane and cyclohexene
- 4 mL of 0.01 mol L^{-1} potassium permanganate ($KMnO_4$) solution
- 5 mL of bromine (Br_2) water
- 2 mL of 2 mol L^{-1} sulfuric (H_2SO_4) acid
- Distilled water
- 4 test tubes and test-tube rack
- 4 graduated droppers
- 5 mL measuring cylinder

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Cyclohexane and cyclohexene are toxic.	Avoid contact with skin and inhalation of vapours. Wear gloves and a laboratory coat. Use in a fume hood. Wash your hands at the end of the experiment.
Bromine water is poisonous and corrosive.	Avoid contact with skin and inhalation of vapours. Wear gloves and a laboratory coat. Use in a fume cupboard. Wash your hands at the end of the experiment.
Sulfuric acid is corrosive.	Wear gloves and personal protective equipment. Avoid contact with skin. Wash your hands at the end of the experiment.
Hexane, cyclohexane and cyclohexene are highly flammable.	Ensure no flame sources are present near either of these chemicals.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

Part A Oxidation reactions with acidified $KMnO_4$ solution

1. Label three test tubes, one for each hydrocarbon.
2. Place 1 mL of each hydrocarbon into the corresponding test tube.
3. In a clean test tube mix 4 mL of $KMnO_4$ solution and 2 mL of H_2SO_4.
4. Add 1 mL of the $KMnO_4/H_2SO_4$ solution to each of the test tubes containing the hydrocarbons.
5. Shake gently and observe for 5 minutes.
6. Dispose of the solutions in a chemical waste jar as directed by your teacher. Do not pour down the sink.
7. Rinse the test tubes and droppers with distilled water.

Part B Addition and substitution reactions with bromine

8. Place 1 mL of each hydrocarbon into the corresponding test tube.
9. Add 1 mL of Br_2 to each test tube.
10. Shake gently and observe for 5 minutes.
11. If a change is noted, add another 1 mL of Br_2 to that test tube and observe.
12. Dispose of the solutions in a chemical waste jar as directed by your teacher. Do not pour them down the sink.

Results

Record the results in a table similar to the one below.

Reagent		Hexane	Cyclohexane	Cyclohexene
Acidified $KMnO_4$ solution	After addition			
	After 5 min			
Br_2	After addition			
	After 5 min			

Analysis of results

1. Which of the hydrocarbons were readily oxidised by the acidified $KMnO_4$ solution?
2. Which reacted with the bromine solution?
3. Write the equation for any reaction that occurred with bromine.

Conclusion

State in your own words the difference between the reactivities of alkanes and alkenes.

REACTION

Watch this video showing the reaction of an alkane and alkene with bromine water.

EXPLANATION

Visit this website to read an explanation of the chemistry of the reaction between an alkene and potassium permanganate.

QUESTION SET 6.2

Remembering

1 Give the general formula for:
- **a** alkanes.
- **b** alkenes.
- **c** alkynes.

2 Explain the difference between saturated and unsaturated compounds.

3 What is the difference between a chain hydrocarbon compound and a cyclic hydrocarbon compound in terms of:
- **a** structure?
- **b** reactivity?

Understanding

4 What is the difference between a geometric isomer and a structural isomer?

5 Which of the following is an alkane, which is an alkene and which is an alkyne? Explain your choice.
- **A** C_6H_{10}
- **B** C_6H_{12}
- **C** C_6H_{14}
- **D** C_6H_{16}

6 Draw a structural formula for:
- **a** propane.
- **b** 2-octene.
- **c** 1-butyne.
- **d** 3-hexyne.

7 Explain why the physical properties of alkanes, alkenes and alkynes are similar but their chemical properties are different.

8 Name the following compounds.
- **a** C_5H_8
- **b** C_4H_{10}
- **c** C_9H_{18}

9 Distinguish between substitution and addition reactions.

Applying

10 **a** Draw the structural formula and name the straight chain isomers of C_5H_{10}.
- **b** Draw and name the *cis* and *trans* isomers of 2-pentene.

11 Write balanced equations for the:
- **a** combustion of pentyne.
- **b** reaction of ethane with chlorine gas (under UV light).
- **c** reaction of 2-butene with water.
- **d** reaction of ethyne with bromine.

Analysing

12 A certain gaseous hydrocarbon is bubbled through bromine. The bromine is not decolorised. What can you conclude about the unknown hydrocarbon?

RULES FOR NAMING ORGANIC COMPOUNDS

Visit this website for an explanation of the rules for naming organic compounds.

6.3 Branched chain hydrocarbons

So far only straight-chain alkanes, alkenes and alkynes have been considered. These are compounds in which all the carbon atoms are in one string so no carbon atom is attached to more than two other carbon atoms.

Many carbon compounds contain branched chains. In branched chain compounds, at least one carbon atom is attached to more than two other carbon atoms.

Naming branched alkanes

Branched alkanes and their derivatives are named according to the following rules.

1 The end of the name tells which hydrocarbon family the compound belongs to. Alkanes always end in -ane.

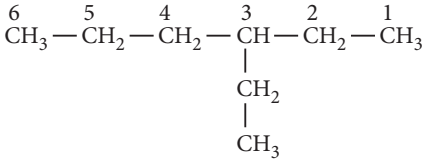
2 Determine the longest continuous carbon chain and use the name of the corresponding alkane. (This chain may not necessarily be drawn in a straight line.) This chain is the main chain and represents the 'parent' structure. For example, if the longest chain had six carbon atoms, the parent structure would be hexane.

3 Other atoms or groups of atoms attached to the main (parent) chain are **substituents** and form 'branches'. If the substituent is a carbon group, then it is called an alkyl group. The name of the alkyl group is based on the number of carbon atoms and has the ending -yl. For example, a substituent group CH_3CH_2— would be called ethyl.

No. of C atoms	1	2	3	4	5	6	7	8	9	10
Stem	meth-	eth-	prop-	but-	pent-	hex-	hept-	oct-	non-	dec-

Other common substituents are F (fluoro), Cl (chloro), Br (bromo), I (iodo) and NO_2 (nitro).

4 Number the carbon atoms in the main (parent) chain so the branch or branches have the lowest possible number/s.

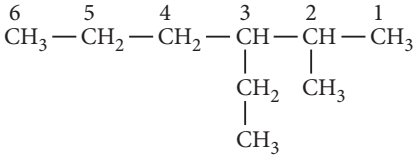


5 The position at which the group is attached to the main (parent) chain is specified by the number of the carbon to which it is attached. (The number is separated by a hyphen.)

In the example above, the branch is 3-ethyl and the compound is 3-ethylhexane. (Note: The alkane name is written as one word.)

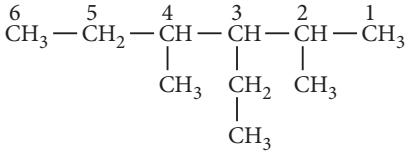
6 List the names of the substituents in alphabetical order (ignoring di-, tri- etc.).

In the example below, there are two branches 3-ethyl and 2-methyl. The 3-ethyl group is listed before the 2-methyl. Words and numbers are separated by a hyphen.



The name of this compound is 3-ethyl-2-methylhexane.

7 Where more than one substituent of the same type is present use the prefixes di (two), tri (three), tetra (four) and penta (five) etc. (Numbers are separated by a comma.)

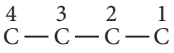


The above compound contains two methyl groups so will contain dimethyl as part of the name, which is 3-ethyl-2,4-dimethylhexane.

Drawing structural isomers

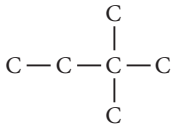
Drawing structural isomers given the systematic name is quite simple.

1 Use the main name to draw the longest carbon chain and number the chain of carbon atoms starting from 1 at an end of the chain (which end does not matter).
For example, in 2,2-dimethylbutane the main chain is butane and the carbon atoms are numbered 1–4.

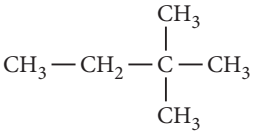


2 Identify the substituents that form the branches and the carbon atoms they are attached to.
In 2,2-dimethylbutane, there are two methyl groups, both attached to carbon number 2.

3 Add the substituent group/s to the parent chain.



4 Add hydrogen atoms to complete the structure. (Check that each carbon atom has four bonds.)





NAMING ALKANES

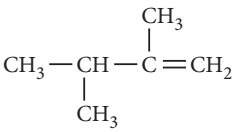
Watch this video, which explains the naming of alkanes with branches.

Naming branched chain alkenes and alkynes

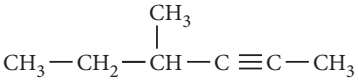
Branching can occur in most classes of organic compounds. To name compounds that have a double or triple bond, the following rules must be added to those for naming alkanes.

1 When naming alkenes and alkynes, the longest continuous carbon chain containing the carbon–carbon double or triple bond becomes the main (parent) chain. The name corresponding to the alkane stem with the ending -ene or -yne forms the main name.

2 Branched alkenes and alkynes are named in a similar way to branched alkanes except the lowest number is assigned to the double or triple bond and *not* the substituent group.



2,3-Dimethyl-1-butene



4-Methyl-2-hexyne



PRACTICE

Visit this website for more practice on naming hydrocarbons.

QUESTION SET 6.3

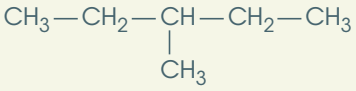
Remembering

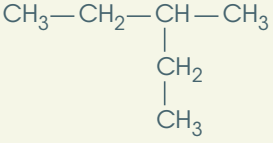
1 Explain how the parent name of a compound is determined.

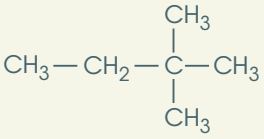
2 What is the main difference between numbering an alkane parent chain and numbering an alkene parent chain?

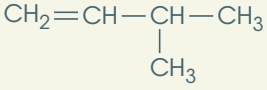
Applying

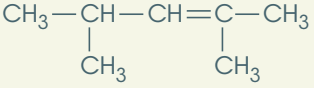
3 Name the following compounds

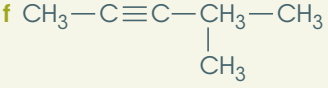
a 

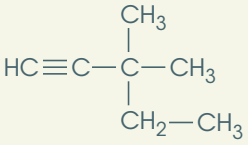
b 

c 

d 

e 

f 

g 

4 Draw the structural formulas of:

a 2-methylpentane.

b 2,3-dimethylbutane.

c 3-ethyl-3-methylhexane.

d 2-methyl-2-pentene.

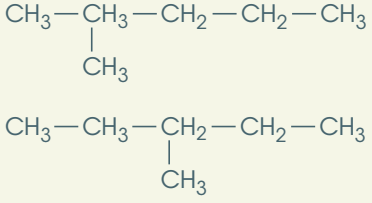
e 3,3-dimethyl-1-butene.

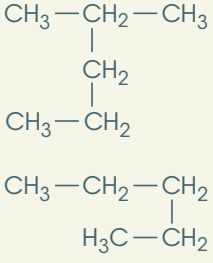
f 4-methyl-2-pentyne.

g 4,6-dimethyl-2-heptyne.

h 2,3-dimethyl-2-butene.

5 Which of the following pairs represent structural isomers?

a 

b 

Analysing

6 Draw the structural isomers for 2-pentene, indicating the *cis* and *trans* isomers if they exist.

7 The following compounds have been named incorrectly. Draw their structural formulas and give the correct names.

a 3-Ethylbutane

b 1-Methyl-4-propylhexane

c 3-Methyl-3-butene

d 2-Ethyl-2-methyl-3-butyne

6.4 Aromatic hydrocarbons

The group known as aromatic compounds originally got their name because many of them have a strong smell (aroma). They all contain a ring or groups of rings of six carbon atoms linked together in a special way.

Many of these compounds were originally derived from plant oils. Today, the source of many of the aromatic hydrocarbons is coal tar.

WOW

Aromatics and cancer

In 1775, a British physician investigating the high incidence of cancer in chimney sweeps hypothesised that the soot was the cause. By the 1930s, it was known that the combustion of wood and coal produced aromatic hydrocarbons so the soot from the chimneys contained large numbers of these compounds and it was shown that these compounds were carcinogenic (cancer causing).

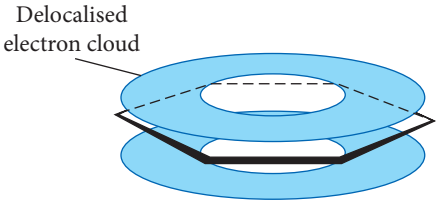
The simplest and also the parent compound of this family is benzene. It is a colourless liquid with molecular formula C_6H_6 so it must be an unsaturated molecule. The structure is a six-sided flat ring with all bond angles being 120°. The carbon atoms are joined in a regular hexagon with one hydrogen atom attached to each carbon. Figure C6.13 shows a space-filling model of benzene.



◀ Figure C6.13
A space-filling model of benzene

On the basis of this representation, it was thought that benzene contained alternating single and double bonds so should undergo addition reactions similar to the alkenes and cycloalkenes. However, this rarely happens. The reactions of benzene are also completely different from those of other double-bonded hydrocarbons.

Further investigation of the benzene ring found that all the carbon–carbon bonds were the same length, which is somewhere between a single bond and a double bond. This can be explained if the electrons of the double bond are spread out around the ring of carbon atoms making a cloud of **delocalised electrons** above and below the ring as shown in Figure C6.14. This is similar to the delocalisation of electrons found in the structure of metals.



◀ Figure C6.14
Bonding in benzene

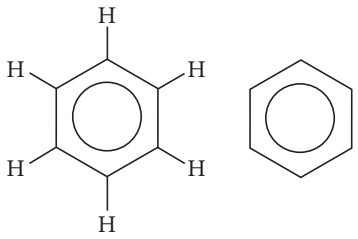
WOW

Kekulé's dream

August Kekulé is credited with solving the puzzle of the bonding in benzene. It is said he had a dream in which a dancing snake formed a ring and bit its own tail. When he woke up, he worked out the structure of benzene, thus solving one of the biggest puzzles in 19th century chemistry.

In chemical structures, the benzene ring is usually represented in either of the two forms shown in Figure C6.15.

Figure C6.15 ▶ Different ways of drawing benzene



To see why delocalised electrons are important in making conducting polymers, refer to Context 4, 'Polymer chemistry', page 95.

The cyclic delocalisation of electrons in the benzene molecule makes it extremely stable. Benzene tends to undergo reactions in which the stable ring is preserved because reactions that disrupt the bonding due to the delocalised electrons are less favourable and will only occur at higher temperatures and under more vigorous conditions.

Most reactions of benzene are **substitution** reactions (like alkanes) where one or more of the hydrogens are replaced by a different functional group.

QUESTION SET 6.4

Remembering

1. What is the main characteristic of aromatic compounds?
2. Write the formula and draw the structure of the simplest member of the aromatic family.
3. Explain why benzene is extremely stable.

Analysing

4. Would you expect benzene to be soluble or insoluble in water? Justify your response by referring to intermolecular bonding.
5. Draw the structure of the new compound formed if one of the hydrogens on the benzene ring was substituted with a methyl group.

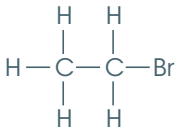
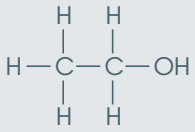
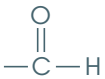
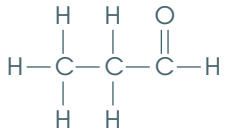
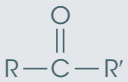
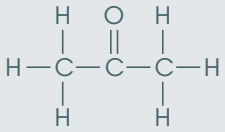
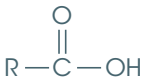
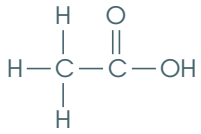
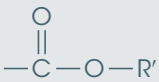
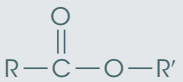
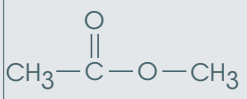
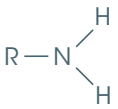
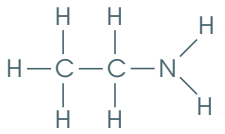
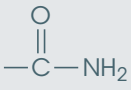
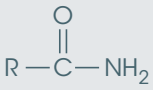
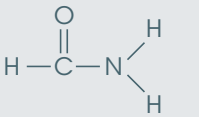
6.5 Functional groups

A group or family of organic compounds has similar properties. Substances within a particular family contain a specific atom or group of atoms called a functional group. For example, compounds containing the —OH (hydroxyl) functional group are called alcohols. Alcohols have many common properties because the hydroxyl group is the most reactive part of the molecule and so compounds with this group will undergo similar types of reactions.

Table C6.5 lists important functional groups. In the general formula, the symbols R and R′ are used to represent different alkyl groups.

Not all these functional groups are part of this course of study, but you can refer to this table if you come across a functional group with which you are unfamiliar. The remainder of this chapter will focus on alcohols, carboxylic acids, esters, amines and amides.

Table C6.5 Functional groups

Class	Suffix	Functional group	General formula	Example	Name of example
Haloalkane	-ane	Halogen —F, —Cl, —Br, —I	R—X		Bromoethane
Alcohol	-ol	—OH	R—OH		Ethanol
Aldehyde	-al				Propanal
Ketone	-one				Propanone
Carboxylic acid	-oic acid				Ethanoic acid
Ester	alkyl -oate				Methyl ethanoate
Amine	-amine	—NH_2			Ethanamine
Amide	-amide				Methanamide

QUESTION SET 6.5

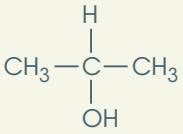
Remembering

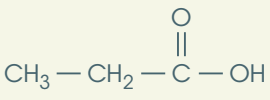
1 Explain why classes of organic compounds are based on functional groups.

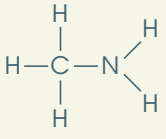
2 Describe what is meant by a functional group.

Understanding

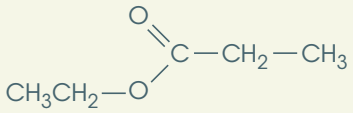
3 Identify the functional group in each of the following compounds.

a 

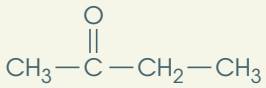
b 

c 

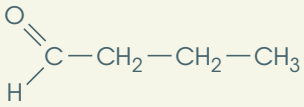
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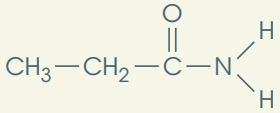
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6.6 Alcohols

Ethanol or ethyl alcohol is the most commonly known member of the alcohol family. It is also one of the most widely used compounds of carbon. Its major uses are:

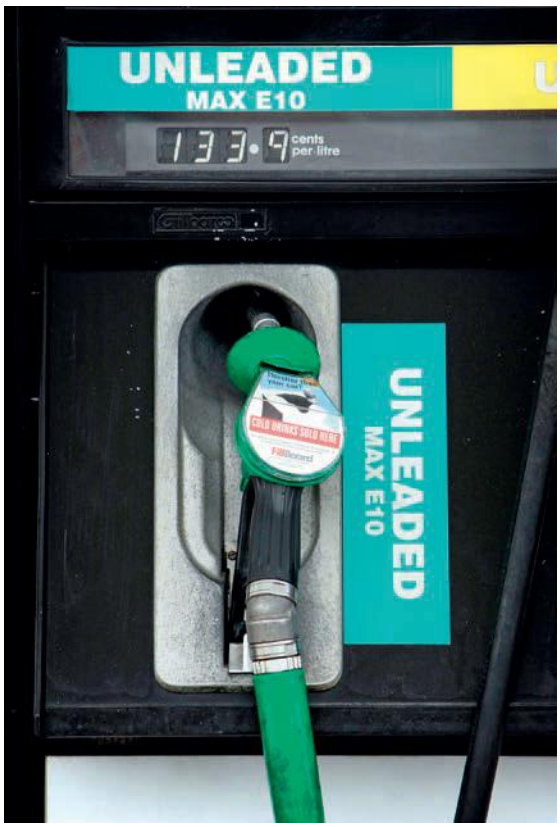
- in beverages such as wine, beer and spirits
- as an additive to petrol or alternative fuel for motor vehicles
- as a solvent in many products, including medicines, antiseptics and household cleaners
- as a reactant and solvent in industry for the manufacture of many products, including plastics, adhesives, pharmaceuticals and perfumes.

However, ethanol is only one member of the family of organic compounds called alcohols. The alcohol functional group is the hydroxyl group —OH and, as shown in Table C6.4, alcohols are represented by the general formula ROH.

Alcohols have the general formula $C_nH_{2n+1}OH$. The simplest alcohol is CH_3OH, which is methanol or methyl alcohol. Ethanol or ethyl alcohol, or more simply 'alcohol' as it is commonly referred to, is CH_3CH_2OH.

The name given to each alcohol clearly reflects its relationship to the alkane. It is simply a substitution of one H on an alkane by an —OH group.

The names, formula, melting and boiling points of the simplest alcohols are shown in Table C6.6.



Nic Gibson/Newspix

Figure C6.16 ▶ Ethanol is an additive in petrol.

Table C6.6 Names, formulas, melting points and boiling points of the simplest alcohols

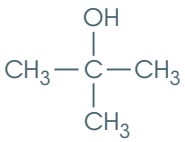
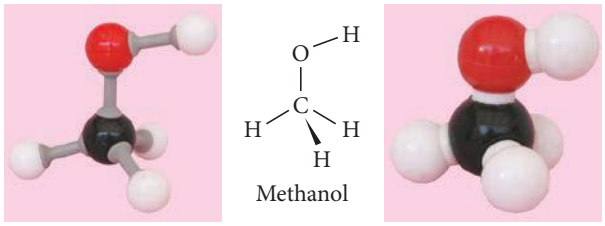
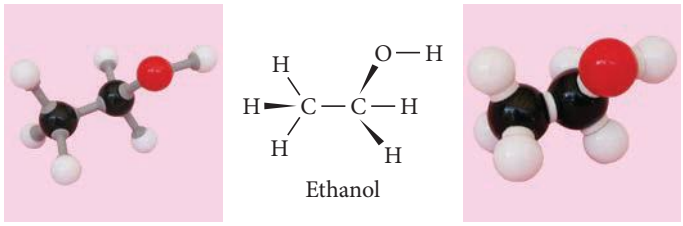
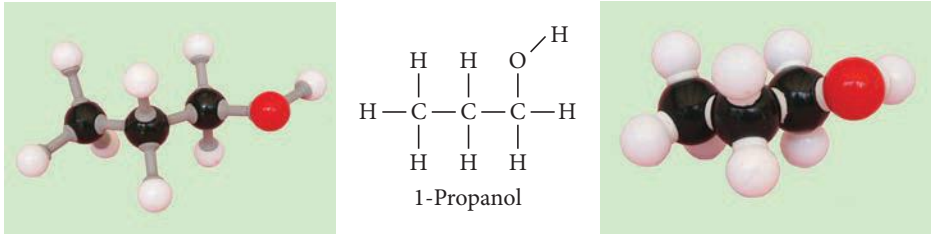
Name	Formula	Melting point (°C)	Boiling point (°C)
Methanol	CH_3OH	−98	65
Ethanol	CH_3CH_2OH	−114	78
1-Propanol	$CH_3CH_2CH_2OH$	−126	97
2-Propanol	$CH_3CHOHCH_3$	−89.5	82
1-Butanol	$CH_3CH_2CH_2CH_2OH$	−90	118
2-Butanol	$CH_3CHOHCH_2CH_3$	−115	99.5
2-Methyl-2-propanol		26	83
1-Pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	−79	138

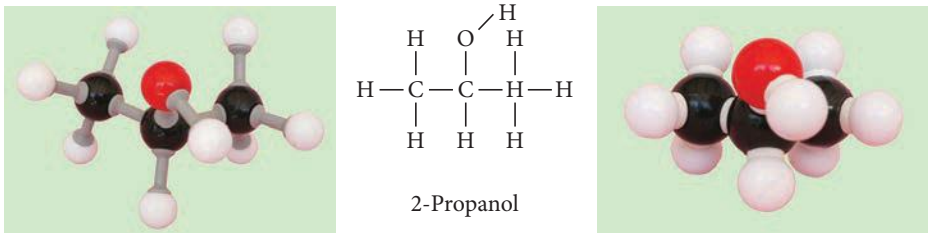
Figure C6.17 shows ball and stick, structural and space-filling models for methanol and ethanol whereas Figure C6.18 shows the two isomers of propanol. As you can see from the diagrams of propanol, there is isomerism in alcohols.





◀ **Figure C6.17**
Ball and stick, structural and space-filling models for methanol and ethanol





◀ **Figure C6.18**
Ball and stick, structural and space-filling models for 1-propanol and 2-propanol

Naming alcohols

To name an alcohol:

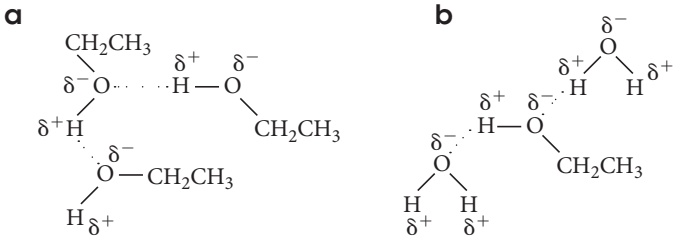
1 identify the longest carbon chain containing the —OH group
2 delete the 'e' of the parent alkane and add -ol; for example, ethane becomes ethanol
3 number the carbon atoms of the main chain from the end that produces the smallest number for the —OH group
4 add a number to the prefix to denote the position of the —OH group; for example, 2-butanol
5 name any alkyl groups as for branched alkanes.

Properties of alcohols

The presence of the highly electronegative oxygen atom means the C—O and O—H bonds are very polar. This means that hydrogen bonding can occur in alcohols. These strong intermolecular forces mean that alcohols have a higher melting and boiling point compared to their corresponding alkanes and alkenes.

The high polarity also means that the —OH group can form hydrogen bonds with water so the simpler alcohols are readily soluble in water, unlike alkanes and alkenes. However, as the carbon chain becomes longer, the molecule becomes more non-polar because the COH part becomes small compared to the longer alkyl chain, so solubility in water decreases with increasing chain length.

Figure C6.19 ▶
Hydrogen bonding: a) in liquid ethanol, and b) between ethanol and water



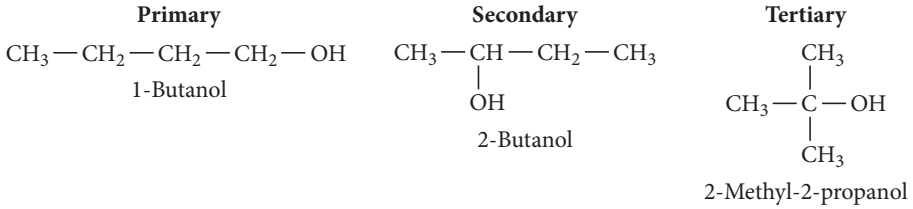
Types of alcohols

Alcohols can be classified according to the number of carbon atoms attached to the carbon bearing the —OH group.

- A **primary alcohol** is one in which one carbon atom is bonded to the carbon atoms attached to the —OH group.
- A **secondary alcohol** is one in which two carbon atoms are bonded to the carbon attached to the —OH group.
- A **tertiary alcohol** is one in which three carbon atoms are bonded to the carbon attached to the —OH group.

Figure C6.20 shows primary, secondary and tertiary alcohols with the molecular formula C_4H_9OH.

Figure C6.20 ▶
Primary, secondary and tertiary alcohols



The three different groups of alcohols have different physical properties and chemical reactivity. This is because the strength of the hydrogen bonding in alcohols depends on the extent to which the —OH group is available for bonding. When the —OH group is on the end of the carbon chain, as in primary alcohols, it is more available for bonding than when it is surrounded by alkyl groups in tertiary alcohols. This means that the boiling points decrease from primary to secondary to tertiary alcohols, as can be seen in Table C6.6.

This also applies to their chemical reactivity. The most vigorous reaction with sodium occurs with a primary alcohol while the least vigorous is with the tertiary alcohol. Similarly, primary

alcohols are more readily oxidised by a strong oxidising agent such as potassium permanganate than secondary alcohols, whereas tertiary alcohols are not oxidised.

Alcohols contain the hydroxyl (—OH) functional group and can be classified as primary, secondary or tertiary. Their properties and reactivity are related to their classification.

Preparation of alcohols

Alcohols can be prepared in a number of ways. One of the most common ways of obtaining ethanol is through **fermentation**. In this process, yeast organisms consume sugars present in fruits such as grapes, sugar cane and grains, and produce ethanol. The equation for the fermentation of glucose ($C_6H_{12}O_6$) is:

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

To see more about fermentation in wine making, refer to Context 1, 'Wine', page 5.

WOW

Methanol and blindness

Methanol is toxic to humans so high concentrations are lethal. Methanol is a by-product of fermentation with more produced in fruit fermentation than in grains due to the presence of pectins. Typically, there will be a small amount in wines. Higher methanol concentrations may be produced if fermenting occurs at high temperatures or a pectin enzyme is added. Professional winemakers monitor methanol concentrations to ensure they remain low. This is because the body's metabolic pathways that break down ethanol to make it harmless turn methanol into methanal, which is metabolised into methanoic acid. The cells of the optic nerve are extremely sensitive to methanoic acid, which is why blindness is closely associated with methanol poisoning.

Ethanol is not the only widely used alcohol, so a number of processes are used to synthesise alcohols.

The most common commercial method is the hydration of an alkene. This is an addition reaction. In the process, an alkene reacts with water in the presence of an acid such as sulfuric acid to produce an alcohol.

For example:

$$\underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2(g)} + H_2O(g) \rightarrow \underset{\text{2-Butanol}}{CH_3CH_2CHOHCH_3(l)}$$

When H–OH gets added across a carbon–carbon double bond, the H nearly always gets attached to the carbon with the most hydrogens already attached to it.

Reactions of alcohols

Combustion

Alcohols undergo combustion. They burn readily in air to produce carbon dioxide and water. For example:

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

Dehydration

Alcohols also undergo dehydration by losing water to form alkenes when heated with concentrated sulfuric or phosphoric acids. (This is the reverse of alcohol preparation.) For example:

$$\underset{\text{2-Butanol}}{CH_3CH_2CHOHCH_3(l)} \rightarrow \underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2(g)} + H_2O(g)$$

2-Butene is also formed in the dehydration reaction. Which isomer gets formed is a matter of chance.

Reaction with sodium

Alcohols react with sodium to form an **alkoxide** anion (RO^-) and hydrogen gas. This is a similar reaction to the one between sodium and water but is less vigorous.

$$2ROH + 2Na \rightarrow 2RO^-Na^+ + H_2$$

For example:

$$\underset{\text{Ethanol}}{2CH_3CH_2OH(l)} + \underset{\text{Sodium}}{2Na(s)} \rightarrow \underset{\text{Sodium ethoxide}}{2CH_3CH_2O^-Na^+(aq)} + \underset{\text{Hydrogen}}{H_2(g)}$$

In this reaction, the alcohol acts as an acid. The alkoxide produced is a strong base and is the conjugate of the weak acid, which is the alcohol. The alkoxide readily reacts with water to form the original alcohol and produce OH^- ions.

MAIN REACTIONS OF ALCOHOLS

Visit this website to understand more about alcohols.

For example:

$$CH_3CH_2O^-(aq) + H_2O(l) \rightarrow CH_3CH_2OH(aq) + OH^-(aq)$$

Oxidation

Alcohols readily undergo oxidation with strong oxidising agents such as acidified permanganate or dichromate solutions.

a Primary alcohols are oxidised to form aldehydes, which are in turn oxidised to form carboxylic acids. Table C6.5 (page 297) shows the aldehyde and carboxylic acid functional groups.

These general reactions can be shown below. The [O] above the arrow in the equation indicates an oxidation process has occurred.

$$R\text{–}CH_2OH \xrightarrow{[O]} R\text{–}CHO \xrightarrow{[O]} R\text{–}COOH$$

The following example shows the oxidation of ethanol to the aldehyde ethanal, then the further oxidation of ethanal to ethanoic acid using acidified potassium dichromate as the oxidising agent. (The oxidation and reduction half-reactions can be derived from the overall reactions given.)

$$\underset{\text{Ethanol}}{3CH_3CH_2OH(aq)} + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow \underset{\text{Ethanal}}{3CH_3CHO(aq)} + 2Cr^{3+}(aq) + 7H_2O(l)$$

$$\underset{\text{Ethanal}}{3CH_3CHO(aq)} + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow \underset{\text{Ethanoic acid}}{3CH_3COOH(aq)} + 2Cr^{3+}(aq) + 4H_2O(l)$$



To see how oxidation of alcohol affects wine, refer to Context 1, 'Wine', page 21.

Aldehydes are easily oxidised to form carboxylic acids so the final product will not contain any aldehyde; it will contain only the carboxylic acid. A sample of an aldehyde can be obtained if an excess of the alcohol is used and the aldehyde is distilled off as soon as it forms.

The excess of the alcohol means that there is not enough oxidising agent present to carry out the second stage. Removing the aldehyde as soon as it is formed means that it does not get oxidised.

The overall equation for the oxidation of ethanol to ethanoic acid can be obtained by adding the two equations above together:

$$\underset{\text{Ethanol}}{3CH_3CH_2OH(aq)} + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow \underset{\text{Ethanoic acid}}{3CH_3COOH(aq)} + 4Cr^{3+}(aq) + 11H_2O(l)$$

This can represented generally as:

$$R\text{–}CH_2OH \xrightarrow{[O]} R\text{–}COOH$$



To learn about polymers based on alcohols, refer to Context 4, 'Polymer chemistry', page 92.

b Secondary alcohols are oxidised to form ketones, which cannot be further oxidised. So the final product in the oxidation of a secondary alcohol is a ketone. (The ketone functional group is shown in Table C6.5.) Acidified permanganate and dichromate both oxidise secondary alcohols. The general equation for the oxidation of a secondary alcohol is shown below.

$$RCHOHR' \xrightarrow{[O]} RCOR'$$

The half and overall equations for the oxidation of 2-propanol are:

$$5CH_3CHOHCH_3(aq) \rightarrow 5CH_3COCH_3(aq) + 10H^+(aq) + 10e^-$$

$$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$$

$$\underset{\text{2-Propanol}}{5CH_3CHOHCH_3(aq)} + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow \underset{\text{Propanone}}{5CH_3COCH_3(aq)} + 2Mn^{2+}(aq) + 8H_2O(l)$$



REVIEW REACTIONS

Visit this website to revise the oxidation of alcohols.

c Tertiary alcohols are not oxidised unless the conditions are drastic because this would involve a large amount of energy to break a C—C bond.

When dichromate is used as the oxidising agent, the orange $Cr_2O_7^{2-}$ ion is reduced to green Cr^{3+}. This test can be used to identify the presence of primary or secondary alcohols or aldehydes. With a tertiary alcohol or a ketone, there would be no change.

Alcohols react with carboxylic acids to form esters. The general equation for this reaction is shown below. These reactions will be discussed later in this chapter.

$$\underset{\text{Carboxylic acid}}{R\text{—}\overset{\overset{O}{\|}}{C}\text{—}OH} + \underset{\text{Alcohol}}{R'OH} \rightarrow \underset{\text{Ester}}{RC\text{—}\overset{\overset{O}{\|}}{C}\text{—}OR'} + \underset{\text{Water}}{H_2O}$$

EXPERIMENT 6.2

DISTINGUISHING BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS (TEACHER DEMONSTRATION)

You will investigate the reactions of primary, secondary and tertiary alcohols with an oxidizing agent and with sodium to identify a way of distinguishing between the three groups.

Aim

To examine and compare the reactions of primary, secondary and tertiary alcohols

Materials

- 10 mL of ethanol, 1-butanol, 2-butanol, 2-methyl-2-propanol
- 5 mL of 0.1 mol L^{-1} sodium dichromate ($Na_2Cr_2O_7$) solution
- 5 mL of 0.01 mol L^{-1} potassium permanganate ($KMnO_4$) solution
- 5 mL of 6 mol L^{-1} H_2SO_4
- 4 very small pieces of Na
- Hot plate or water bath
- Thermometer
- 250 mL beaker
- 5 large test tubes
- 10 mL measuring cylinder
- Metal tongs
- Dropper
- Tweezers

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Sodium dichromate is toxic.	Avoid contact with skin and inhalation of vapours. Wear gloves and a laboratory coat. Use in a fume hood. Wash your hands at the end of the experiment.
Sodium metal oxidises rapidly in air and is highly reactive with water. Contact will burn the skin.	Wear gloves and a laboratory coat. Do not allow contact with water to occur. Handle sodium only with tweezers and use only a very small amount.
Sulfuric acid is corrosive.	Wear gloves and personnel protective equipment. Avoid contact with the skin. Wash your hands at the end of the experiment.
Alcohols are highly flammable.	Ensure no flame sources are present in the location of these chemicals.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

Part A Reactions with oxidising agents

Reaction with permanganate (MnO_4^-)

1. Pour 2 mL of each of the alcohols into separate, labeled test tubes.
2. In a separate test tube mix 4 mL of potassium permanganate solution with 1 mL of sulfuric acid.
3. Using the dropper place 4–5 drops of the permanganate mixture into each of the test tubes containing the alcohols.
4. Record your observations, including smell.
5. Dispose of the solutions in a chemical waste jar as directed by your teacher. Do not pour them down the sink.

Reaction with dichromate ($Cr_2O_7^{2-}$)

1. Prepare a water bath at a temperature of 80°C.
2. Pour approximately 2 mL of each of the alcohols into separate, labeled test tubes.
3. In a separate test tube mix 4 mL of sodium dichromate solution with 2 mL of sulfuric acid.
4. Place 1 mL of this solution into each of the test tubes containing the alcohols, shaking gently to mix.

5 Place the test tubes in the water bath for 5 minutes. Shake gently occasionally.
6 Record any changes including smell.
7 Dispose of the solutions in a chemical waste jar as directed by your teacher. Do not pour them down the sink.

Part B Reaction with sodium metal

1 Pour 2 mL of each of the alcohols into separate, dry, labelled test tubes.
2 Obtain four very small pieces of sodium from your teacher. Place one piece in each test tube.
3 Carefully observe the rates at which the reactions occur. Record your observations.
4 Dispose of the solutions in a chemical waste jar as directed by your teacher. Do not pour them down the sink.

Results

Draw up a table to record your observations.

Analysis of results

1 Rank the alcohols in order of reactivity.
2 Generalise this to a statement about the relative reactivities of primary, secondary and tertiary alcohols.
3 Write the names and formulas of the products formed where reactions took place.
4 Write separate balanced equations for the oxidation of ethanol by MnO_4^- to ethanal and ethanoic acid.
5 Write a general equation for the reaction of alcohols with sodium.

Conclusion

State in your own words the difference between the reactivities of the different classes of alcohols.

Extension

Use your understanding of the reactions of ethanol to use these tests to distinguish between alcoholic and non-alcoholic wine.

QUESTION SET 6.6

Remembering

1 Name and give the structure of the alcohol functional group.
2 Explain why:
- **a** alcohols are soluble in water.
- **b** solubility decreases as the alkane chain of the alcohol gets longer.

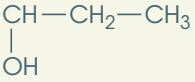
3 Describe the three classes of alcohols and give an example of each class.

Understanding

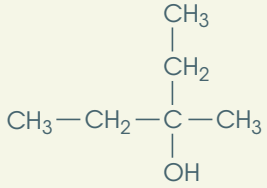
4 Explain how and why the properties of alcohols vary with the class of alcohol.
5 Name the following compounds.

a $CH_3CH_2CH_2CH_2CH_2CH_2OH$

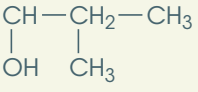
b



c



d



6 Draw the structural formula of:
- **a** 2-propanol.
- **b** 3-methyl-1-butanol.
- **c** 2,3-dimethyl-3-pentanol.
- **d** 3-methyl-4-octanol.

Applying

7 Name and draw the structural formulas of two isomers of an alcohol with the molecular formula C_4H_9OH.

8 Write equations for the following reactions, naming the products.

- a Dehydration of 3-pentanol
- b Hydration of 1-propene
- c Combustion of 2-butanol
- d Reaction with sodium of 1-hexanol

9 Identify the final product (if any) from oxidising:

- a 2-butanol.
- b methanol.
- c 2-methyl-2-hexanol.

10 Write balanced equations for the oxidation of:

- a 1-propanol to propanal by acidified permanganate solution.
- b 2-pentanol by acidified dichromate solution.

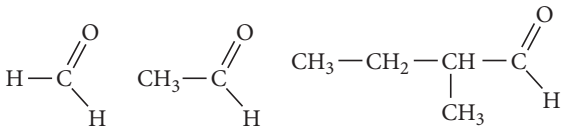
6.7 Aldehydes and ketones

Compounds containing a carbon atom double bonded to an oxygen atom are called **carbonyl compounds**. Both aldehydes and ketones are carbonyl compounds.

Aldehydes are carbon compounds that contain a carbon–oxygen double bond at the end of the carbon chain. The compound is represented by the general formula:



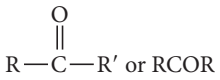
Examples of aldehydes are:



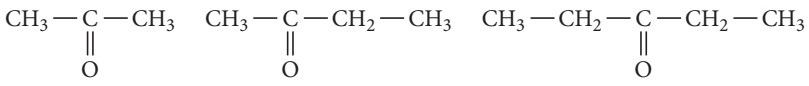
Methanal Ethanal 2-Methylbutanal

Methanal, HCOH, commonly known as formaldehyde, is the simplest aldehyde. Methanal is used in vast quantities in the manufacture of plastics. The first plastics, known as Bakelite, were made by using phenol and formaldehyde.

Ketones differ from aldehydes in that the C=O can be located on any carbon except those at the ends of the hydrocarbon chain. The compounds have the general formula:



Examples of ketones are:



Propanone Butanone 3-Pentanone

Propanone is widely used as a solvent and is commonly known as acetone.

Naming aldehydes and ketones

Aldehydes are named by replacing the 'e' on the name of the hydrocarbon containing the C=O group with the suffix 'al'.

To name an aldehyde:

1 identify the longest carbon chain containing the —CHO group
2 delete the 'e' of the parent alkane and add —al; for example, ethane becomes ethanal
3 number the carbon atoms of the main chain from the aldehyde (No number is needed for the aldehyde functional group.)
4 name any alkyl groups as for branched alkanes.

Ketones are named by replacing the 'e' on the name of the hydrocarbon containing the C=O group with the suffix 'one'.

To name a ketone:

1 identify the longest carbon chain containing the C=O group
2 delete the 'e' of the parent alkane and add —one; for example, propane becomes propanone
3 number the carbon atoms of the main chain from the end that results in the smallest number for the C=O group
4 add a number to the prefix to denote the position of the C=O group; for example, 2-pentanone
5 name any alkyl groups as for branched alkanes.

Properties of aldehydes and ketones

Oxygen is more electronegative than carbon so has a strong tendency to attract electrons in the carbon–oxygen bond. This makes the carbon–oxygen double bond highly polar. Because of this polarity, dipole–dipole forces exist between molecules in aldehydes and ketones.

As a result, aldehydes and ketones have higher boiling points than hydrocarbons of similar molecular mass. However, the boiling points are lower than those of the corresponding alcohols.

Small aldehydes and ketones are soluble in water, but as chain length increases, solubility in water decreases. This is because the longer hydrocarbon component of the molecule gets in the way of the polar attraction between the water molecule and the polar C=O functional group.

Reactions of aldehydes and ketones

Aldehydes can be prepared by the oxidation of primary alcohols with acidified dichromate or acidified permanganate as the oxidising agent.

Aldehydes are readily oxidised with the same reducing agents to produce carboxylic acids. Both of these reactions are discussed in section 6.6.

Ketones can be prepared by the oxidation of secondary alcohols as shown in section 6.6. Unlike aldehydes, ketones are not further oxidised by acidified permanganate or dichromate solutions.

QUESTION SET 6.7

Remembering

1 **a** Describe the difference between the aldehyde and ketone functional groups.
b What difference does this make in the preparation of these compounds?

2 What type of intermolecular bonding do these compounds have?

Understanding

3 Why are smaller aldehydes and ketones soluble in water but larger molecules are not?

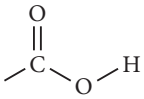
4 Draw the structural formula of:
   a butanal.
   b 4-methylpentanal.
   c 3-hexanone.
   d 3-methyl-2-pentanone.
5 Name the following compounds.
   a CH_3CHO
   b CH_3CH_2CHCHO (with CH_3 branch)
   c $CH_3CH_2CH_2COCH_3$
   d $CH_3CH_2CHCH_2COCH_2CH_3$ (with CH_2CH_3 branch)

6.8 Carboxylic acids

Carboxylic acids can be found throughout nature. A few of the more common acids are formic (methanoic) acid, which is a chemical defence for some ants and is injected when they bite. Acetic acid is found in vinegar, propanoic acid is found in cheese, butanoic acid is in spoiled butter, citric acid is found in citric fruits and lactic acid is found in milk and other dairy products. Many of these carboxylic acids have strong unpleasant odours.

Synthetic compounds manufactured from carboxylic acids include soap, some plastics, pharmaceuticals and herbicides.

Carboxylic acids contain the carboxyl functional group —COOH, which is always present at the end of the molecule. The configuration of these four atoms in the carboxylic acid group must be:

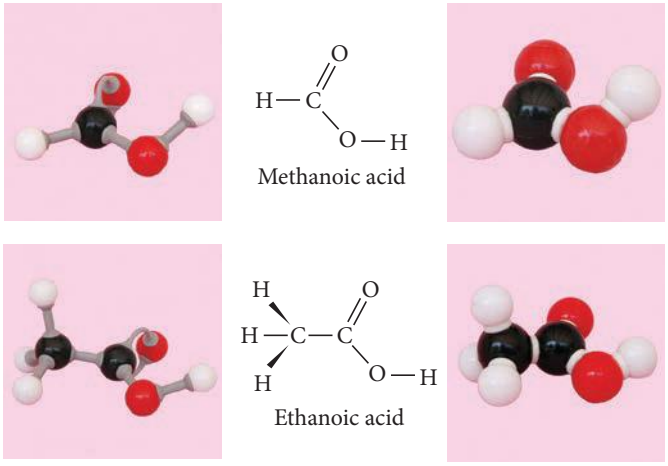


This group has the general formula $C_nH_{2n+1}COOH$. Carboxylic acids are weak acids (see Chemistry Chapter 2). The simplest carboxylic acids are shown in Figures C6.22 and C6.23 with their systematic names.



Visuals Unlimited/naturepl.com

▲ **Figure C6.21**
Ants inject acid when they bite.

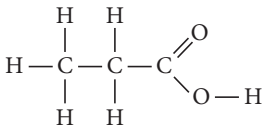


◀ **Figure C6.22**
Ball and stick, structural and space-filling models for methanoic acid and ethanoic acid

The three acids shown in Figures C6.22 and C6.23 are also referred to by common names. The common name for methanoic acid is formic acid, for ethanoic acid is acetic acid and for propanoic acid is propionic acid.

Figure C6.23 ▶ Ball and stick, structural and space-filling models for propanoic acid





Propanoic acid



Naming carboxylic acids

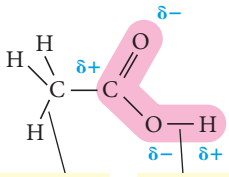
To name a carboxylic acid:

1 identify the longest carbon chain containing the —COOH group
2 delete the 'e' of the parent alkane and add -oic acid; for example, ethane becomes ethanoic acid
3 number the carbon atoms of the main chain from the acid group (No number is needed for the acid functional group, which is always at the end of the carbon chain so will be always be 1.)
4 name any alkyl groups as for branched alkanes.

Carboxylic acids are compounds that contain the functional group —COOH, regardless of what else is attached to it, and exhibit the common properties of acids.

Properties of carboxylic acids

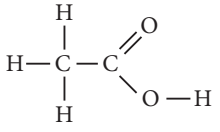
The carboxylic acid group is monoprotic. This is because the only H atom that can react with a base is the one in the —COOH group. This is shown in Figure C6.24. They undergo the usual reactions of acids.



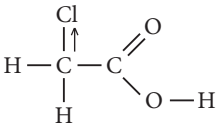
This bond is virtually non-polar and so this H cannot be drawn away and leave its electron behind.

This bond is highly polar. Since the electrons spend more time near the O atom, H can be drawn away by a base and leave its electron behind.

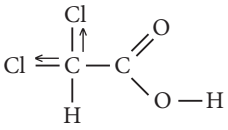
▲ Figure C6.24 Why ethanoic acid can only act as a monoprotic acid



Ethanoic acid



Chloroethanoic acid



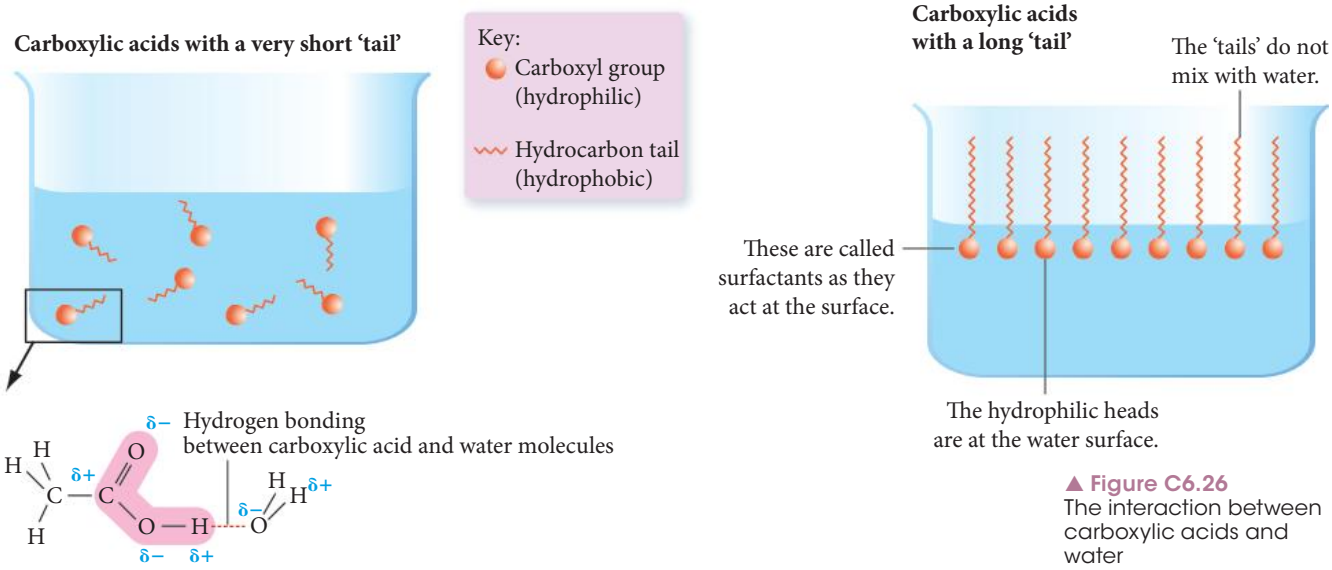
Dichloroethanoic acid

Figure C6.25 ▲ Relative acid strength of substituted carboxylic acids: as the number of electronegative atoms (e.g. chlorine) increases, so does the strength of the acid.

The strength of a carboxylic acid can be increased by substituting a highly electronegative atom such as a halogen onto the hydrocarbon chain. As the number of substituted atoms increases, so does the strength of the acid. This is because the strong electron-attracting power of the substituent weakens the oxygen–hydrogen bond in the —OH group and makes it easier to form H^+ ions. This is shown in Figure C6.25; dichloroethanoic acid is almost 3000 times stronger than ethanoic acid.

The presence of the —OH and —C=O groups makes the carboxyl group polar, so carboxylic acids can form strong hydrogen bonds. As a result, similar to alcohols, carboxylic acids have higher melting points, boiling points and densities than other organic groups of similar size and molecular mass.

The smaller carboxylic acids are soluble in water because the strong polar carboxyl group is **hydrophilic** ('water loving') and is therefore able to hydrogen bond to water. However, as the size of the **hydrophobic** ('water hating') carbon chain increases, solubility decreases. This is shown in Figure C6.26.



▲ **Figure C6.26**
The interaction between carboxylic acids and water

WOW

Fatty acids

Fatty acids are carboxylic acids with a carbon chain of three or more carbon atoms. Two fatty acids are essential to human body processes (linoleic and linolenic) and must be part of a balanced diet. The main source of linoleic acid is polyunsaturated vegetable oils. This acid is important because it is involved in many processes that lead to the production of important compounds called prostaglandins. A lack of linoleic acid and other fatty acids in the diet can lead to scaly skin, poor growth and weight gain.

Reactions of carboxylic acids

Reaction with reactive metals

Carboxylic acids react with reactive metals to produce a salt and hydrogen gas.

For example:

$$Mg(s) + 2CH_3COOH(aq) \rightarrow Mg^{2+}(aq) + 2CH_3COO^-(aq) + H_2(g)$$

Reaction with base (neutralisation)

Carboxylic acids react with a base to produce a salt and water in a neutralisation reaction.

For example:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq) + H_2O(l)$$

Reaction with carbonate

Carboxylic acids react with carbonates to produce a salt plus carbon dioxide and water.

For example:

$$2CH_3COOH(aq) + Na_2CO_3(aq) \rightarrow 2Na^+(aq) + 2CH_3COO^-(aq) + CO_2(g) + H_2O(l)$$

Esterification

Esterification is the reaction of a carboxylic acid with an alcohol to produce an ester. This reaction will be considered in section 6.9.

MAIN REACTIONS OF CARBOXYLIC ACIDS

Visit this website to understand more about the reactions of carboxylic acids.

QUESTION SET 6.8

Remembering

1 Identify the carboxylic acid functional group.
2 Explain why smaller carboxylic acids are soluble in water but those with longer chains are not.
3 List the general reactions characteristic of acids that carboxylic acids undergo.

Understanding

4 Draw the structural formula of:
- **a** ethanoic acid.
- **b** heptanoic acid.
- **c** 2-methylpropanoic acid.
- **d** 2,3-dimethylbutanoic acid.

5 Name the following compounds
- **a** $HOOC—CH_2—CH_2—CH_2—CH_3$
- **b** $CH_3—CH_2—COOH$
- **c**
$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—COOH$$

Applying

6 **a** What would you observe when sodium carbonate powder is added to a solution of propanoic acid?
b Write a balanced equation for the reaction.
7 Write equations for the reaction of:
- **a** butanoic acid and sodium hydroxide.
- **b** methanoic acid and sodium metal.

Analysing

8 Explain how you would distinguish between two clear liquids knowing one is propanol and the other is propanoic acid.
9 Carboxylic acids can be produced by the oxidation of primary alcohols. What alcohol would you need to oxidise to produce butanoic acid?
10 Carboxylic acids have higher boiling points than alcohols of corresponding mass. Explain in terms of bonding why this is so.

6.9 Esters

Esters are an important group of organic compounds found in a wide range of biological systems. They have pleasant fruity odours and are responsible for the flavours and fragrances of many fruit and flowers. Solid animal fats and animal and vegetable oils are natural esters.

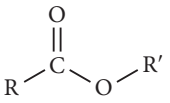


Lucie Lang

Figure C6.27 ▶ Bee's wax is a natural ester

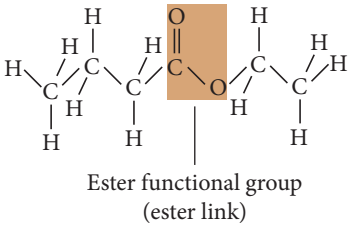
As well as being widespread in nature, esters are commonly used in industry. Esters can be synthesised easily and they are produced synthetically for use as artificial flavouring and colourings. Several billion kilograms of polyesters are produced annually to make a wide variety of products including fabrics, and bottles.

Esters have a similar structure to carboxylic acids except that an alkyl group is attached to the oxygen rather than a hydrogen atom. The general formula for an ester is:



where R and R′ represent alkyl groups.

An example of an ester is shown in Figure C6.28. This ester is found in pineapples, peaches and apricots. The ester group formed is also an **ester link** because it links the two molecules that react, an alcohol and a carboxylic acid, to produce it.



◀ **Figure C6.28**
The ester – ethyl butanoate

Synthesising esters

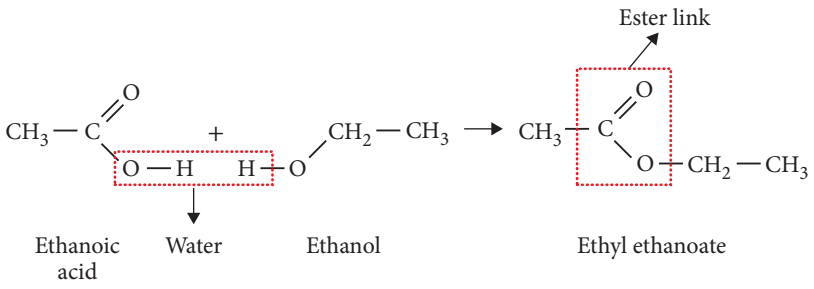
Esters are produced by the reaction between an alcohol and a carboxylic acid. This esterification reaction is moderately slow at room temperature. To speed up the reaction, the mixture is heated in the presence of an acid catalyst, usually concentrated sulfuric acid.

Esterification is the reaction in which a carboxylic acid reacts with an alcohol to produce an ester.

The general reaction can be written as:

$$R{-}COOH + HO{-}R' \rightarrow R{-}COO{-}R' + H_2O$$

Notice that in this reaction a water molecule is produced. A reaction in which the functional groups of two molecules join and a small molecule is released is called a **condensation reaction**. Figure C6.29 shows the reaction between ethanoic acid and ethanol to produce ethyl ethanoate and water.



◀ **Figure C6.29**
Reaction between ethanoic acid and ethanol

To see an important synthesis of esters, refer to Context 4, 'Polymer chemistry', page 96.

Naming esters

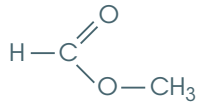
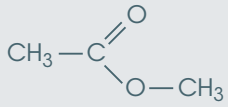
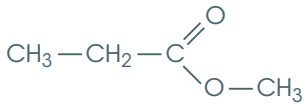
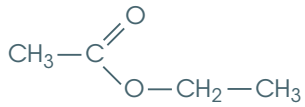
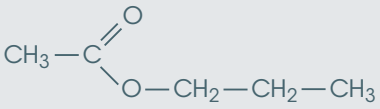
The names of esters are two words.

1. The first part of the name is the alkyl group. This comes from the alcohol from which the ester was formed.
2. The second part of the name comes from the carboxylic acid used in the ester formation. The end of the acid name is changed from -oic acid to -oate.

To see which esters are found in wine, refer to Context 1, 'Wine', page 19.

Table C6.7 Formula and properties of some common esters

Methanoate and ethanoate are the IUPAC preferred names for the common names formate and acetate.

Name	Formula	Molecular mass	Boiling point (°C)	Solubility in water (g/100 g water)
Methyl methanoate (formate)		60	32	24
Methyl ethanoate (acetate)		74	57	6.7
Methyl propanoate		88	80	7.3
Ethyl ethanoate (acetate)		88	77	7.5
Propyl ethanoate (acetate)		102	102	2

ESTERS AND PERFUMES

Watch this video, which discusses the synthesis of esters and perfume manufacture.

Properties of esters

The presence of the C—O and C=O makes esters polar substances. However, esters tend to be liquids at room temperature and their boiling points are much lower than for carboxylic acids of similar mass. This is because their main intermolecular forces are dipole–dipole forces, which are weaker than the hydrogen bonding in carboxylic acids and alcohols.

Most esters are not very soluble in water (Table C6.7) due to the lack of hydrogen bonding and the presence of hydrophobic alkyl groups. However, they are soluble in organic solvents. Many esters are also used as solvents in industry. For example, ethyl ethanoate is a common solvent in nail polish remover.

Reactions of esters

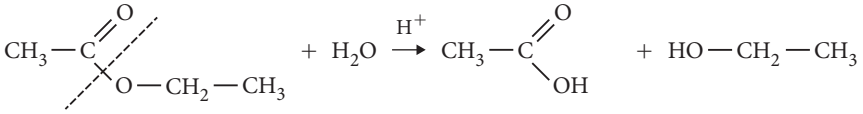
The reaction for forming esters is reversible and so under certain conditions esters can react with water to produce the original acid and alcohol from which they were made. This reaction with water is called **hydrolysis**.

Hydrolysis can occur under both acid and alkaline conditions.

Under acid conditions (in the presence of heat and sulfuric acid), the reaction is:

$$R—COO—R' + H_2O \rightarrow R—COOH + HO—R'$$

For example:

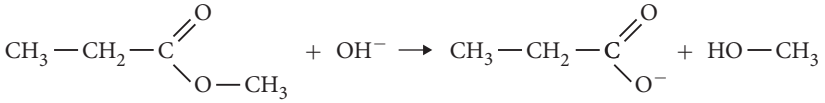


Ethyl ethanoate — Ethanoic acid — Ethanol

Under alkaline conditions (in the presence of heat and sodium hydroxide), the reaction is:

$$R—COO—R' + OH^- \rightarrow R—COO^- + HO—R'$$

For example:



Methyl propanoate — Hydroxide ion — Propanoate anion — Methanol

MAIN REACTIONS OF ESTERS

Visit this website to understand more about esters.

To see how hydrolysis affects ester products, refer to Context 4, 'Polymer chemistry', page 97.

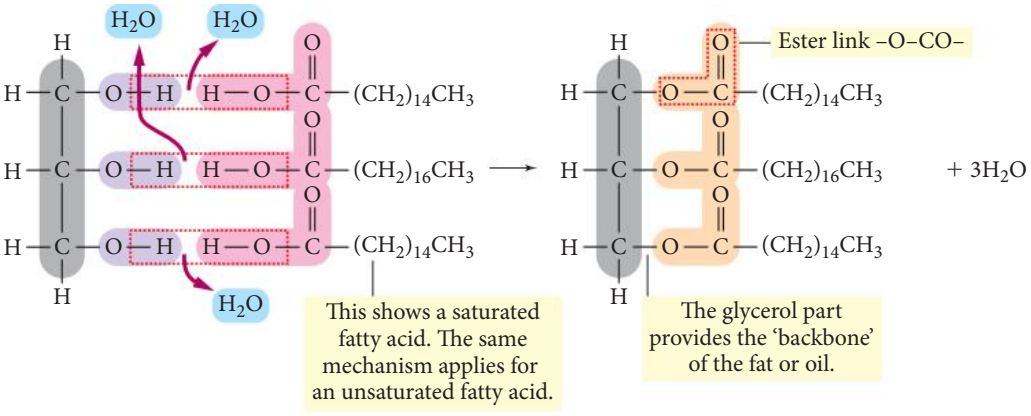
The reaction between an ester and a hydroxide ion to form an alcohol and a carboxylate anion is called **saponification**. This reaction is used for making soap.

Fats and oils

Fats and oils are natural esters and belong to the organic family called **triglycerides**. If they are solid at room temperature, then they are called fats. If they are liquid at room temperature, then they are oils. They are generally formed when 1,2,3-propanetriol (a propane molecule in which an —OH is joined to each carbon), commonly known as glycerol, reacts with saturated and unsaturated fatty acid molecules. The glycerol molecule makes up the backbone of the molecule and the fatty acids make up the tail.

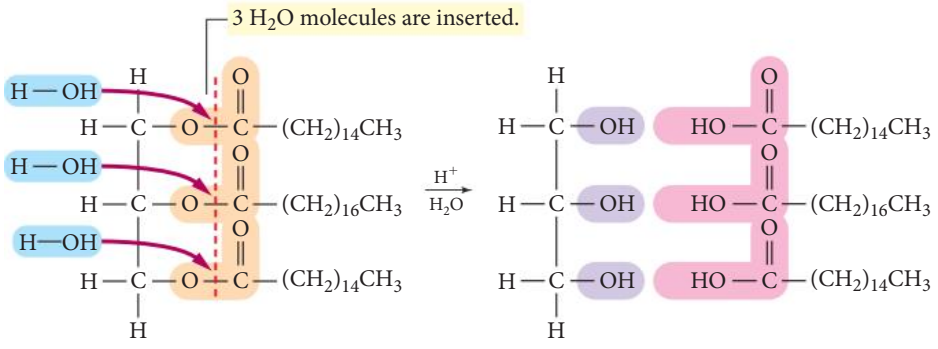
Each of the three alcohol groups in glycerol forms an ester link with a fatty acid, eliminating a water molecule in the process. As for all esters this esterification reaction is reversible through hydrolysis, and during digestion these fats and oils are broken down to glycerol and fatty acids. These reactions are shown in Figure C6.30.

Production of a fat



Glycerol + 3 Fatty acids $\xrightarrow[\text{reaction}]{\text{Condensation}}$ Triglyceride + $3H_2O$

Hydrolysis of a fat



Triglyceride + $3H_2O$ $\xrightarrow[\text{reaction}]{\text{Hydrolysis}}$ Glycerol + 3 Fatty acids

◀ **Figure C6.30**
The production and hydrolysis of a fat

To see how this is used in making soap, refer to Chemistry section 9.5, page 419.

EXPERIMENT 6.3

PREPARATION OF SOME ESTERS

Aspirin (acetylsalicylic acid), oil of wintergreen (methyl salicylate) and ethyl ethanoate (used in nail polish remover) are all esters.

Many esters have pleasant fruity odours and occur widely in nature as perfumes and flavouring agents. Esters account for the distinctive odours of many fruits such as bananas, oranges, pineapples and strawberries.

Esters can be synthesised in the laboratory. The low rate of reaction between these compounds means that heat needs to be applied. The commonly used method is by a technique called refluxing in which the mixture is boiled and the vapours produced are condensed and collected.

Aim

To prepare some different esters

Materials

- 5 g salicylic acid
- 10 mL each of methanol, ethanol, 1-butanol, 1-octanol, 3-methyl-1-butanol, 3-methyl-1-pentanol, 10 mL each of glacial acetic acid (ethanoic acid), pentanoic acid, butanoic acid, propanoic acid, concentrated sulfuric acid (18 mol L^{-1})
- Hot plate
- 6 test tubes
- 2 × 500 mL beakers
- 10 mL graduated cylinder
- Dropper
- Thermometer
- Distilled water
- Ice in an ice bath

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Concentrated sulfuric acid and acetic acid are corrosive.	Wear gloves and personal protective equipment. Avoid contact with the skin. Wash your hands at the end of the experiment.
Alcohols are highly flammable.	Ensure no flame sources are present in the location of these chemicals.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

You may choose your own combinations of alcohol and carboxylic acid to produce the esters. Different combinations will produce different esters.

1. Half fill the 500 mL beaker with water. Place this on the hotplate and heat to approximately 60°C. This is your water bath.
2. Number six test tubes. To each of the test tubes add 1 mL of an alcohol and 1 mL of a carboxylic acid from those provided. If using solid salicylic acid, add approximately 1 g.
3. Add 3–5 drops of concentrated sulfuric acid to each test tube.
4. Heat the test tubes in the water bath for 15 minutes.
5. Remove the test tubes from the water bath and cool them in an ice bath.
6. Add 5 mL of distilled water to each test tube. The ester is less dense than water so it will form a layer on top of the water.
7. Carefully smell the ester and note the odour.
8. Dispose of the chemicals according to your teacher's instructions.

Results

Record your observations and copy and complete the following results table.

Test tube	Alcohol	Carboxylic acid	Odour	Ester (name and formula)
1				
2				
3				
4				
5				
6				

Analysis of results

1 Compare your results with those of others in your class and construct a table listing all the esters produced and their odours.

2 **a** Write a general equation for the esterification reaction.

b Write balanced equations to represent two of the esters you produced.

3 Compare the relative solubility of alcohols, carboxylic acids and esters and then suggest why water was added in step 6.

QUESTION SET 6.9

Remembering

1 Draw the ester functional group.

2 Explain why esters have little solubility in water yet the two chemical groups from which they are formed are quite soluble.

Understanding

3 Describe the relationship between esterification and hydrolysis.

4 Draw the structural formula for:

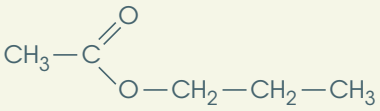
a ethyl propanoate.

b propyl methanoate.

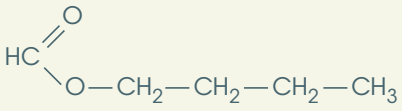
c butyl ethanoate.

5 Name the following compounds.

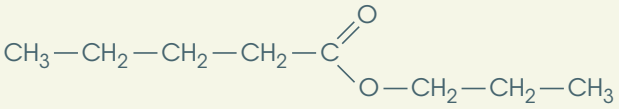
a



b



c



6 Draw the structural formulas for three esters of molecular formula $C_4H_8O_2$ and name them.

Applying

7 Write equations for the reaction between the following compounds and name the esters produced.

a 1-Propanol and ethanoic acid

b 1-Pentanol and butanoic acid

8 Explain why the solubility of esters decreases as the molecular weight increases.

9 Write a balanced equation for the acid hydrolysis of pentyl propanoate.

10 Write a balanced equation for the saponification of propyl butanoate and name the products of the reaction.



REVISION

Revise alcohols, carboxylic acids and esters.

6.10 Amines and amides

Amines have a wide range of uses as catalysts and solvents and in the manufacture of dyes, medicines and polymers, so they are an extremely important family of organic compounds. Amines are also found widely in nature as amino acids, which are the building blocks of proteins.

An amide is formed when an amine reacts with a carboxylic acid. Polyamides are an important group of synthetic plastics.

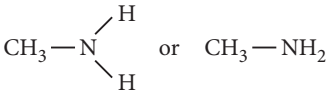
Urea, an important compound in industry and living systems, is a carbamide with the formula $H_2N—CO—NH_2$. It has two NH_2 groups attached to a carbonyl (C=O) group. Urea was the first organic compound to be synthesised from inorganic starting materials, thus showing organic compounds were part of a chemical system and could be produced outside living things.

Amines

The **amine** (or amino) functional group is $—NH_2$. Amines are compounds in which one or more atoms of hydrogen in ammonia (NH_3) are replaced by a carbon-containing group such as an alkyl group. Alkyl amines are represented by the general formula RNH_2. Some simple amines are shown in Figure C6.31.

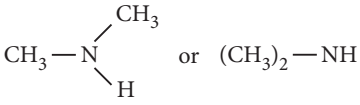
Figure C6.31 ▼
Some simple amines

a



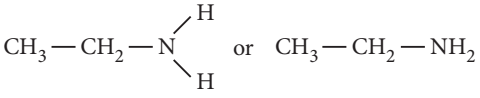
Methanamine

b



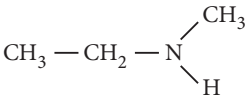
Dimethanamine

c



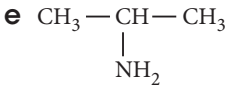
Ethanamine

d



Ethylmethanamine

e



2-propanamine

Amines may be classified as primary, secondary or tertiary depending on the number of alkyl groups attached to the nitrogen. A primary amine has one alkyl group (Figure C6.31a and c), a secondary amine has two alkyl groups attached to the nitrogen (Figure C6.31b) and a tertiary amine has three alkyl groups attached to the nitrogen; for example, $(CH_3)_3N$.

Naming amines

To name a simple amine:

1. identify the carbon chains attached to the N and put them in alphabetical order (using the alkyl name except for the final group) with no spaces
2. delete the 'e' from the last alkane name and add 'amine'. For example, ethane becomes ethanamine (Figure C6.31c). If there is an ethyl chain and a methyl chain, then the name would be ethylmethanamine.
3. add the prefixes di- and tri- if two or three of the alkyl groups are the same (Figure C6.31b).
4. number the carbons on the main chain from the end nearest the amine group. If the amine group is not on the end, its location is shown by stating the number of the carbon to which it is attached at the front of the name; for example, 2-propanamine (Figure C6.31e)
5. name any alkyl group attached to the main carbon chain according to the conventions for naming alkanes.

Properties of amines

Nitrogen is the third most electronegative element after fluorine and oxygen, so the $—NH_2$ functional group is very polar. Primary and secondary amines can form hydrogen bonds due to the presence of N—H bonds within the molecule. Because nitrogen is less electronegative than oxygen, the hydrogen bonds formed by amines are weaker than those formed by alcohols. This results in the boiling

points of amines being lower than those of similar-sized alcohols. The hydrogen bonding means the smaller amines are soluble in water. Tertiary amines cannot form hydrogen bonds because there is no N—H bond in the molecule. Consequently, their boiling points are lower than those of primary and secondary amines and they are generally insoluble in water. Amines also have an ammonia-like smell.

This text will only focus on the reactions of primary amines.

Reactions of primary amines

Reaction with inorganic acids

Amines are weak bases, similar to ammonia from which they are formed. Therefore they will undergo a neutralisation reaction with acids to form a salt and water.

For example:

$$\underset{\text{Methanamine}}{CH_3—NH_2(aq)} + HCl(aq) \rightarrow \underset{\text{Methylammonium chloride}}{CH_3—NH_3^+Cl^-(aq)}$$

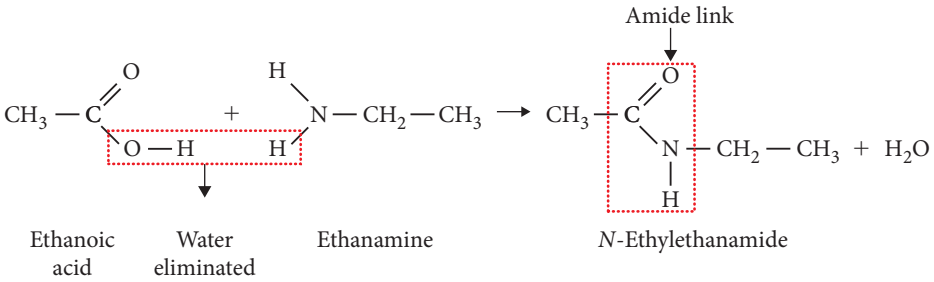
This can be represented generally as:

$$RNH_2(aq) + H^+(aq) \rightarrow RNH_3^+(aq)$$

Reaction with organic acids

Amines react with carboxylic acids in a similar way to the reaction with an inorganic acid. However, under certain conditions amines and carboxylic acids undergo a condensation reaction (eliminating water) to form amides.

For example:



This can be represented generally as:

$$R—COOH + H_2N—R' \rightarrow R—CO—NH—R' + H_2O$$

TUTORIAL

Watch this video tutorial, which explains the naming and reactions of amines.

When the nitrogen is bonded to an alkyl group and one hydrogen, the name of the alkyl group is written first. An N– *is used to indicate that the alkyl group is attached to the nitrogen.*

WOW

Sniffing proteins

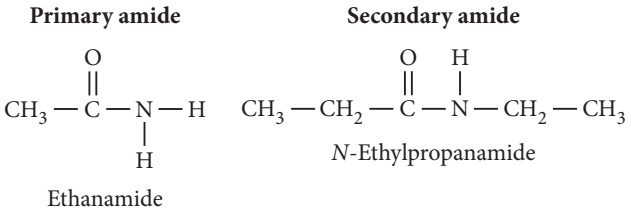
Amines and amides are important biological molecules because they are part of proteins. When an organism dies, its proteins are broken down into many different compounds containing the amino acid functional group. Two of these compounds are putrescine and cadaverine, which have a distinctive, unpleasant odour. In forensic investigations, specially trained sniffer dogs use these odours to locate human remains.

Amides

Amides are derivatives of carboxylic acids and are formed when the —OH group of the acid is replaced by an amine (—NH_2, —NHR′) group. The amide formed is a stable covalent molecule with no acidic or basic properties. Amides all contain the structural unit —CO—NH—, which is shown diagrammatically in Figure C6.34. This amide link occurs in proteins and polyamides. As with amines, amides are classified as primary, secondary or tertiary depending on the number of alkyl chains attached to the nitrogen.

This text will only focus on primary and secondary amides, such as those shown in Figure C6.32.

Figure C6.32 ▶ Primary and secondary amide structure



Naming amides

To name an amide:

1. change the ending of the acid name by replacing '-oic acid' with '-amide'; for example, ethanoic acid becomes ethanamide (Figure C6.32)
2. name any alkyl groups bonded to the nitrogen atom as *N*-alkyl in front of the amide name (Figure C6.32).

RULES

Visit this website for more detailed rules on naming amines and amides.

Preparation of amides

Primary amides are produced in two steps:

1. The carboxylic acid is converted to an ammonium salt using ammonium carbonate. (This is a typical acid–carbonate reaction.) For example:

$$\underset{\text{Ethanoic acid}}{2CH_3COOH(aq)} + (NH_4)_2CO_3(aq) \rightarrow \underset{\text{Ammonium ethanoate}}{2CH_3COONH_4(aq)} + CO_2(g) + H_2O(l)$$

To see where amines and amides are used, refer to Context 4, 'Polymer chemistry' page 99.

2. The resultant mixture is then heated to dehydrate the ammonium salt, producing the amide. For example:

$$CH_3COONH_4(aq) \rightarrow CH_3CONH_2(s) + H_2O(g)$$

Secondary amides are produced by the reaction of a carboxylic acid and primary amine as shown on page 317.

Properties of amides

Amides have both N—H and C=O polar bonds. This means they form hydrogen bonds between the H of one molecule and the O of another, as well as with water. Therefore, most amides are solids at room temperature and their melting points are high for the size of the molecule.

Small amides are soluble in water, but their solubility decreases as the amides get larger or more alkyl groups are attached to the nitrogen.

Reactions of amides

Amides undergo hydrolysis reactions in a similar way to esters. The reaction for forming amides is reversible and so under certain conditions, primary amides can react with water to produce the original acid or acid salt and ammonia from which they were made. Secondary amides will produce the original acid and primary amine.

This reaction can occur under both acid and alkaline conditions:

- Under acid conditions (in the presence of heat and a dilute acid):

$$R—CO—NH_2 + H_2O + H^+ \rightarrow R—COOH + NH_4^+$$

For example:

$$\underset{\text{Ethanamide}}{CH_3—CO—NH_2} + H_2O + HCl \rightarrow \underset{\text{Ethanoic acid}}{CH_3—COOH} + \underset{\text{Ammonium chloride}}{NH_4Cl}$$

- Under alkaline conditions (in the presence of heat and sodium hydroxide):

$$R—CO—NH_2 + OH^- \rightarrow R—COO^- + NH_3$$

For example:

$$\underset{\text{Ethanamide}}{CH_3—CO—NH_2} + NaOH \rightarrow \underset{\text{Sodium ethanoate}}{CH_3—COONa} + \underset{\text{Ammonia}}{NH_3}$$

Other reactions that amides undergo include dehydration and reduction to a primary amine, but they will not be considered here.

QUESTION SET 6.10

Remembering

1 Draw and label the structural units that identify a substance as an amine or amide.

2 Explain why these amines and amides have higher melting and boiling points and are soluble in water.

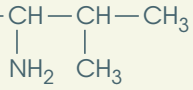
3 Describe the relationship between an amine and an amide.

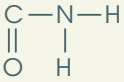
Understanding

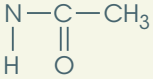
4 Name the following compounds.

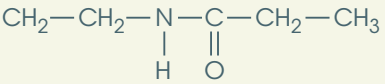
a $CH_3—CH_2—CH_2—NH_2$

b $(CH_3—CH_2)_3N$

c 

d 

e 

f 

5 Draw the structure of:

a hexanamine.

b dipropanamine.

c 2-methyl-3-octanamine.

d propanamide.

e *N*-methylmethanamide.

Applying

6 Write equations for the reactions of:

a propanamide with hydrochloric acid.

b methanoic acid with ammonium carbonate.

c methanoic acid with butanamine.

7 Amides can be hydrolysed under acidic or alkaline conditions. What products could be formed from the hydrolysis of the structure in Question **4d**?

Analysing

8 Explain why tertiary amines are insoluble in water and do not form amides.

9 Why does the solubility of amines and amides decrease as the molecules become larger?

10 You are given two clear solutions – one is an amine and one is an amide. How would you identify which is the amine and which is the amide?

6.11 Tests to distinguish between classes of organic compounds

INFORMATION

Visit this website for more information on tests used to distinguish between classes of organic compounds.

Each class of organic compounds is considered to have its own characteristic molecular structural features that lead to their physical properties and chemical reactions. These properties and reactions can be used to distinguish between and identify different classes of organic compounds. The classes considered in this section are alkanes, alkenes, alcohols, carboxylic acids, esters, amines and amides.

In devising a set of tests to distinguish between different classes of compounds, the most easily identified is usually the starting point.

Some tests that can be performed to determine the class of compound of an unidentified sample are listed in Table C6.8.

Table C6.8 Tests for determining class of organic compound

Class of compound	Test and result
Amines	Test with litmus paper or universal indicator. If the solution is basic, then it is an amine.
Carboxylic acid	Add drops of sodium carbonate solution to the sample. If bubbles of colourless gas form (CO_2), then the solution is a carboxylic acid.
Alcohol	Add granules of calcium chloride to remove any water present, and then add a small piece of sodium. If bubbles of colourless gas form (H_2), then the sample is an alcohol. (Carboxylic acids also react the same way but they will already have been identified.)
Amide	Add NaOH and gently heat the solution. If ammonia is produced, then the solution is an amine, and the pH will change from basic to acidic.
Alkene or alkyne	Add drops of bromine or bromine water to the organic solvent. If the solution loses colour, then a multiple bond is present as it is decolourised by alkenes.
Alkane or ester	If the above tests are negative, then the compound is an alkane or ester. Add a solution of bromine in hexachloroethane and expose it to UV light. If the colour fades, then the compound is an alkane.
Ester	There is no simple test for esters. If the compound has a pleasant smell, then it is probably an ester. Spectroscopy is needed to confirm the presence of this class of compounds.

INVESTIGATION 6.1

DISTINGUISHING BETWEEN CLASSES OF ORGANIC COMPOUNDS

When identifying a compound, the first step is to determine which class of organic compounds the unknown substance belongs to. In this investigation, you will need to identify the class an unknown compound belongs to. You will not be given an alkane or ester because the test and reaction is unsuitable for student use.

What is your aim?

You will need to confirm that the tests you are using work for that class of organic compound before identifying the unknown sample.

What will you need?

Use the information on tests for distinguishing classes of organic compounds (Table C6.8) and previous experiments to consider what equipment you will need.

What are the risks?

Decide on at least one compound from each class to confirm each of the identification tests. Check the Material Safety Data Sheet for this compound.

Refer to safety considerations in other experiments in this chapter.

How will you carry out your investigation?

Use the information on tests for distinguishing classes of organic compounds (Table C6.8) and previous experiments to draw a flowchart to outline the procedure you might follow.

You could further distinguish between alcohol groups using what you learnt in Experiment 6.2.

Write out a step-by-step procedure using the flowchart to help you.

What results will you collect?

Perform the identifying tests on the known compounds you chose to confirm the reactions and record your observations in a table.

Obtain an unknown compound from your teacher and identify its class. If it is found to be an alcohol, then try to determine whether it is primary, secondary or tertiary.

How will you analyse your results?

Write balanced equations for the reactions you used to distinguish between the different classes.

Which class is the most reactive? Which class is the least reactive?

What have you found?

Use your results to justify the identity of the unknown sample.



REVISE

Visit this website to revise naming and reactions of some carbon compounds and to test your knowledge.

CHAPTER CHECKLIST

You should know:

- organic molecules are built on a skeleton of covalently bonded carbon atoms
- the types of atoms present in a molecule and the overall shape in which they are arranged determine in which chemical interactions and reactions the molecule can participate
- organic chemicals can be classified into groups or 'families' of related compounds that share key chemical characteristics
- isomers are compounds with the same molecular formula but different structural formula so have different properties
- the functional groups for alcohols, carboxylic acids, esters, amines and amides
- the characteristic physical properties and chemical reactions for the listed functional groups
- the relationship between bonding, structure and properties for different classes of compounds
- tests for distinguishing between different classes of organic compounds.

You should be able to:

- draw structural formulas for organic compounds
- identify compounds based on their functional group and apply IUPAC naming conventions
- identify and name isomers
- predict the products of chemical reactions involving specified functional groups
- relate structure, bonding and properties for identified classes of compounds
- distinguish between different classes of organic compounds
- distinguish between different groups of compounds based on experimental data
- identify acid–base and oxidation reactions which functional groups undergo
- conduct investigations safely and identify risks.

CHAPTER GLOSSARY

alicyclic (cyclic) hydrocarbon a compound in which the carbon atoms have joined together to form a closed ring structure

aliphatic compound a hydrocarbon consisting of a chain or non-aromatic ring

alkane a chain hydrocarbon with only single carbon–carbon bonds

alkene a chain hydrocarbon with at least one carbon–carbon double bond

alkoxide an anion formed when an alcohol loses the H from the alcohol functional group

alkyne a chain hydrocarbon with at least one carbon–carbon triple bond

amine an organic family in which one or more atoms of hydrogen in ammonia (NH_3) are replaced by a carbon-containing group such as an alkyl group

aromatic hydrocarbon a hydrocarbon containing one or more benzene rings

carbonyl compound a compound containing the carbonyl group —C═O

carboxylic acid an acid with the functional group —COOH

condensation reaction a reaction between two functional groups that results in the release of a small molecule (usually water)

cycloalkane a cyclic hydrocarbon with only single carbon–carbon bonds

cycloalkene a cyclic hydrocarbon with at least one carbon–carbon double bond

cycloalkyne a cyclic hydrocarbon with at least one carbon–carbon triple bond

delocalised electrons valence electrons that are not restricted to specific bonds but which spread over several atoms in a chemical compound

dispersion force weak intermolecular force resulting from momentary dipoles

ester link the link between a carboxylic acid and an alcohol that forms an ester

esterification the reaction of a carboxylic acid with an alcohol to produce an ester

fermentation the process in which yeast consumes sugars in fruit and grains to produce ethanol

functional group a special atom or group of atoms present in the families of organic compounds that imparts particular chemical and physical properties

geometrical isomer an isomer resulting from the presence of a double bond around which carbon atoms cannot rotate, so they differ in the geometric relationship of substituent groups. Such isomers may also be referred to as *cis–trans* isomers

hydrophilic attracting water; 'water loving' and capable of forming bonds with water

hydrolysis reaction with water

hydrophobic more attracted to particles of the same type than to water, usually immiscible with water

inorganic compound a compound that is not organic

organic compound a compound containing carbon (except carbonates, carbon dioxide and carbon monoxide)

primary alcohol an alcohol in which one carbon atom is bonded to the carbon atoms attached to the —OH group

saponification the reaction between an ester and a hydroxide ion to form an alcohol and a carboxylate anion

saturated compound an organic compound with only single bonds between carbon atoms

secondary alcohol an alcohol in which two carbon atoms are bonded to the carbon attached to the —OH group

substituent an atom or group of atoms that takes the place of (substitutes for) hydrogen on a parent carbon in a hydrocarbon molecule

tertiary alcohol an alcohol in which three carbon atoms are bonded to the carbon attached to the —OH group

triglyceride a large molecule formed from the reaction between glycerol and three fatty acids

unsaturated compound an organic compound containing one or more multiple bonds

CHAPTER REVIEW QUESTIONS

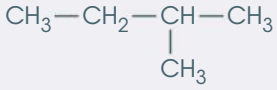
Remembering

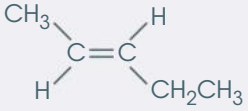
1 Classify each of the following statements as true or false. Rewrite those that are false so they are true.
   - a The class of an organic compound is determined by its functional group.
   - b An organic compound with the —OH group is a carboxylic acid.
   - c Alkanes are more reactive than alkenes.
   - d Esters are produced by the reaction between an alcohol and an alkyne.
   - e The addition of hydrogen to a carbon–carbon double bond produces an alkane.
   - f Only tertiary alcohols can be oxidised to ketones.
   - g An alkyne is a hydrocarbon containing a triple bond.
   - h Primary alcohols are less reactive than secondary alcohols.
   - i An organic compound containing carbon–carbon double or triple bonds is unsaturated.
   - j Carboxylic acids react with carbonates to produce hydrogen gas.
   - k Amines contain the functional group $-NH_2$ and are acidic.
   - l Aldehydes have higher boiling points than the corresponding alkane due to dipole–dipole forces.
   - m Ketones can be oxidised to carboxylic acids.
2 Identify which classes of organic compounds are soluble in water and explain why.
3 Distinguish between an amine and amide in terms of bonding and properties.

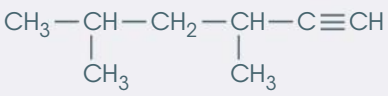
Understanding

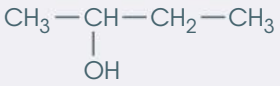
4 Which of the following could be an alkyne?
   - A C_2H_4
   - B C_4H_{10}
   - C C_5H_8
   - D CH_2O

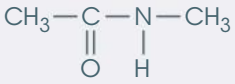
5 Identify the class of organic compound and name each of the following compounds.

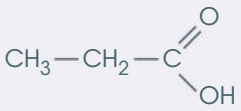
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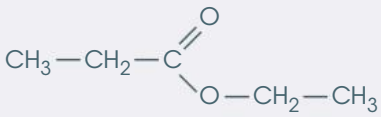
b 

c 

d 

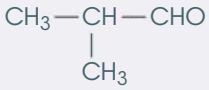
e 

f 

g 

h 

i $CH_3CH_2CH_2COONa$

j 

k $CH_3CH_2CH_2CH_2COCH_2CH_2CH_3$

6 Draw structural formulas for:

a 2-heptanol.

b 4,5-dimethyl-2-hexyne.

c 2-ethylbutanoic acid.

d 2-ethyl-1-hexanol.

e pentanamide.

f propyl butanoate.

g 3-heptanamine.

h *N*-methylpropanamide.

i 2-fluorobutanal.

j 3-methyl-2-butanone.

7 Draw structural formulas for the following and give the systematic names for each.

a All isomers with molecular formula C_3H_8O

b Carboxylic acids or esters with molecular formula $C_3H_6O_2$

8 Compare the intermolecular forces and relative boiling points of the following classes of organic compounds.

a Alkanes and alcohols

b Carboxylic acids and esters

c Amines and amides

9 Ethanol and water readily dissolve in each other (miscible), as do ethanol and hexane. However, water and hexane do not dissolve in each other (immiscible).

a Explain why ethanol is miscible in both water and hexane but water and hexane do not mix.

b Considering your answer to part a, suggest why ethanol is a solvent widely used in industry.

Applying

10 Write equations for the following reactions and name the products.

- **a** The dehydration of 2-butanol
- **b** The hydration of 1-pentene
- **c** 1-Butanol reacting with ethanoic acid
- **d** $CH_3—CH_2—CH_2—CH_2—NH_2 + HCl$
- **e** Ethanamine and butanoic acid

11 A student wanted to prepare the insoluble ester butyl methanoate. What reagents would the student need?

12 Amides can be hydrolysed to different products depending on whether they are a primary or secondary amide. Name and draw the structure of the products formed from the hydrolysis of:

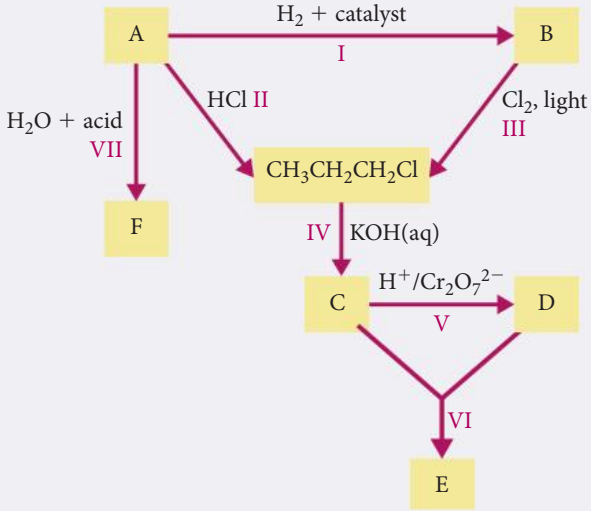
- **a** $CH_3—CH_2—CO—NH_2$
- **b** $CH_3—CO—NH—CH_3$

13 Write the half reactions and overall reaction for the reaction between 2-butanol and an acidified dichromate solution. Name the organic product of this reaction.

14 Copy and complete the flowchart in Figure C6.33. State the type of reactions I–VII.

15 What would you expect to be the final product (if any) from oxidising:

- **a** 2-hexanol?
- **b** propanol?
- **c** 2-methyl-2-pentanol?



▲ Figure C6.33

Analysing

16 Three compounds are known to be 1-propanol, ethanoic acid and methyl methanoate. Their boiling points (but not in that order) are 118°C, 32°C and 97°C. Match the correct boiling point to the compound, giving reasons for your choice.

17 Four bottles containing clear liquids were found on the laboratory shelf, but the labels had fallen off. The missing labels were found on the floor and had the names:
1-hexene (C_6H_{12}), pentane (C_5H_{12}), water (H_2O) and ethanol (C_2H_5OH).

A group of chemistry students was asked to devise a series of tests to identify the contents of each of the four bottles. The students labelled the bottles A, B, C and D and conducted their tests. Their results are shown below.

Bottle	Soluble in water	Flammable	Decolourises bromine in the absence of UV light
A	Yes	No	No
B	No	Yes	Yes
C	No	Yes	No
D	Yes	Yes	No

- **a** Using the information from the tests, identify which bottle contained which chemical, giving reasons for your decision.
- **b** Write balanced equations for the reactions that occurred.

18 What chemical tests would you use to distinguish between the following pairs of compounds?

- **a** 1-Butanol and butanoic acid
- **b** 2-Propanol and 2-methyl-2-propanol
- **c** Heptane and 2-heptene
- **d** Ethyne and ethyl ethanoate
- **e** Propanamine and propanamide

19 A chemist had three liquids – ethanol, butanoic acid and 3-heptyne – but did not know which was which, so called them P, Q and R.

When drops of bromine solution were added to samples of each liquid, P and Q decolorised the bromine but R did not.

When drops of sodium carbonate solution were added to fresh samples of the three liquids, R produced bubbles of colourless gas but P and Q did not.

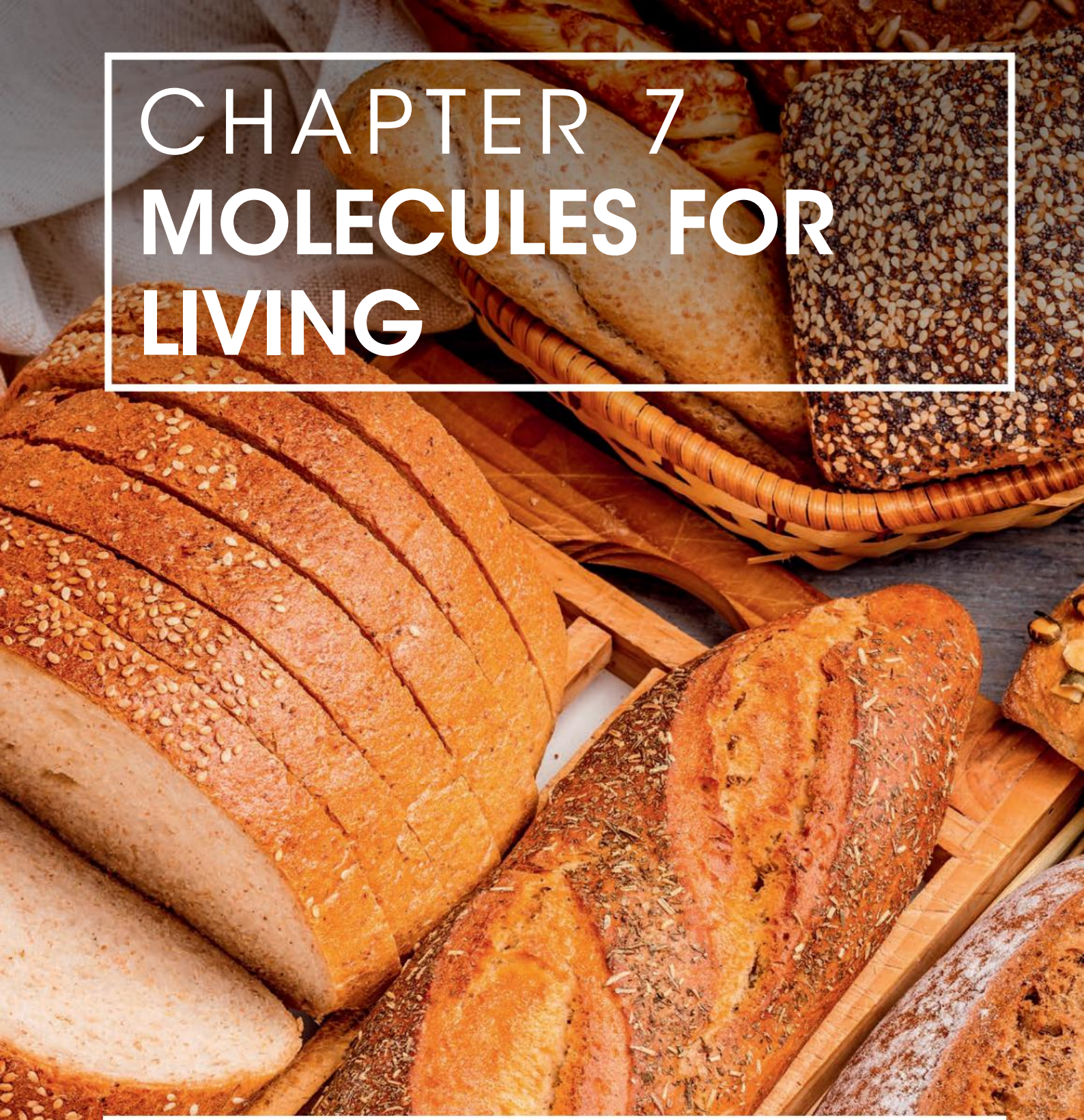
When a piece of sodium metal was added to fresh samples of the three liquids, P and R produced bubbles of gas but Q did not.

Use this information to identify each of P, Q and R, giving equations for the reactions that occurred.

Reflecting

20 A key idea in organic chemistry is that 'structure dictates function'. Explain what you think this means and why it is considered a key idea.

CHAPTER 7
MOLECULES FOR LIVING



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By the end of this chapter you will have covered the following material.

Science Understanding

- Organic materials including proteins, carbohydrates and synthetic polymers display properties including strength, density and biodegradability that can be explained by considering the primary, secondary or tertiary structures of the material (ACSCH129)
- Organic molecules, including polymers, can be synthesised using addition and condensation reactions (ACSCH136)

7.1 Organic molecules in our lives

Apart from the inorganic molecules of water and oxygen, we depend more on organic molecules in every aspect of our lives than inorganic ones. The food we eat, the clothes we wear, the plastics we rely on in everyday products and the fuels that power transport vehicles are all mainly composed of organic compounds. The medicines we use to fight microbes and even the microbes themselves are largely made up of organic compounds.

Although inorganic water is the most abundant chemical in the body, most of the other chemicals are carbon-based organic chemicals. All living things are massive chemical machines composed largely of organic compounds interacting in a watery soup. The membranes of our cells, DNA and the **enzymes** that catalyse the chemical reactions within cells are all organic compounds. Muscles, fat and skin are all based on organic compounds and our bones are formed from a framework of organic compounds in which minerals become embedded.

Life is sustained by organic chemistry and in our daily lives we rely on the products of organic chemistry to maintain our health and lifestyles.

In this chapter, you will consider the synthesis of polymers and fuels along with the structures of synthetic polymers, carbohydrates and proteins.

Figure C7.1 ▶
Levels of structure in collagen

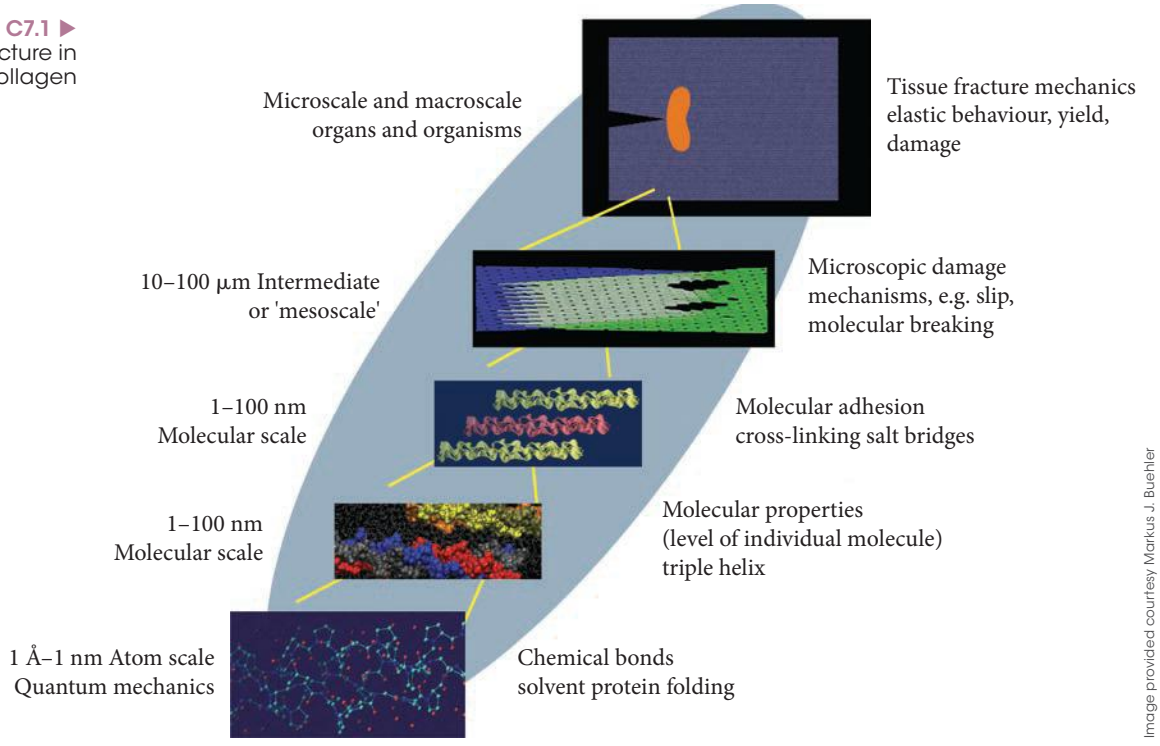


Image provided courtesy Markus J. Buehler

Synthetic polymers

Polymers are giant molecules, often called macromolecules, which form when many smaller molecules, called **monomers**, are joined by covalent bonds. The process of linking monomers together is called **polymerisation**.

The two most common polymerisation reactions are:

- addition polymerisation, which involves an addition reaction
- condensation polymerisation, which involves a condensation reaction.

Polymerisation is a chemical reaction in which many small molecules called monomers link together by covalent bonds to form one large molecule called a polymer.

THERMOPLASTICS AND THERMOSETTING POLYMERS

Visit this website for more examples of thermoplastics and thermosetting polymers.

Polymers may be natural or synthetic. Natural polymers including silk, wool and hair (made of proteins), starch (made of carbohydrate) and DNA are manufactured by living organisms. Synthetic polymers, commonly referred to as plastics, are manufactured in laboratories, or on larger scales in factories.

It is important at this stage to distinguish between synthetic polymers and **plastic**. While all plastics are synthetic polymers, not all synthetic polymers are plastics. Plastics are malleable and pliable and capable of being moulded by heat and pressure. Chemists distinguish between polymers that can be melted and re-formed and those than cannot by using the terms **thermoplastic** and **thermosetting**.



Don Pablo/Shutterstock.com

▲ **Figure C7.2** Plastic drink bottles are made of a thermoplastic polymer so can be easily recycled

Thermoplastic polymers soften on heating and so are easily recycled because they can be melted and remoulded. Thermoplastic polymers are used in plastic bags and plastic wrap (polyethylene), garden hoses (polyvinyl chloride) and soft-drink bottles (polyethylene terephthalate). Thermosetting polymers do not become soft or change shape on heating, so are not easily recycled. These polymers are generally stronger, more chemically resistant and more durable than thermoplastic polymers and are used, for example, in insulating foams (polyurethane), worktop surfaces (melamine) and some older electrical insulators (Bakelite). The differences in these types of polymers are due to the structure and bonding with the polymer.



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◀ **Figure C7.3** Melamine is an example of a thermosetting plastic

WOW

Macromolecules

Organic chemist Hermann Staudinger is known as the father of macromolecular chemistry. In 1922, he proposed that during a chemical reaction he called 'polymerisation' individual repeating units joined together by covalent bonds to form molecules of high molecular weight. His postulate that macromolecules existed was not well received by his colleagues. Despite well-founded scientific evidence, he continued to encounter strong opposition to his ideas for more than 20 years. However, by the end of the 1930s, his concept of macromolecules was gaining acceptance by chemists. In 1953, he was finally acknowledged for his research when he was awarded the Nobel Prize in Chemistry.

ALKANES TO ALKENES

Watch this video showing how alkanes can be made into alkenes.

To see how catalytic cracking relates to the use of the fractions, refer to Context 4, 'Polymer chemistry', page 85.

Starting with ethylene

Ethylene (ethene), which is obtained from crude oil, is the most widely used starting material for making synthetic polymers.

As you learnt in *Nelson Chemistry Units 1 & 2* Context 2, crude oil is a mixture that is separated into its various fractions by fractional distillation. Generally, more petrol is needed than is supplied from the fractional distillation of crude oil so the longer carbon chain fractions are broken into smaller components by **catalytic cracking**. This process uses catalysts called **zeolites**.

Alkanes with 15–25 carbon atoms are broken into two smaller molecules – an alkane and an alkene. The alkene may be further spit into smaller alkenes.

For example:

$C_{15}H_{32} \rightarrow C_{10}H_{22} + C_5H_{10}$

$C_5H_{10} \rightarrow C_2H_4 + C_3H_6$

QUESTION SET 7.1

Remembering

1 Explain the relationship between a monomer and a polymer.
2 What is the difference between a synthetic polymer and a natural polymer?
3 How are thermoplastic polymers different from thermosetting polymers?
4 Explain what occurs during a polymerisation reaction and name two types of polymerisation reactions.

Understanding

5 Write an equation for the catalytic cracking of:
   a butadecane ($C_{14}H_{30}$) into a C_8 alkane and a C_6 alkene.
   b the splitting of the C_6 alkene into two C_3 alkenes.

Analysing

6 What are the advantages of using a catalyst to produce smaller molecules?

7.2 Addition polymers

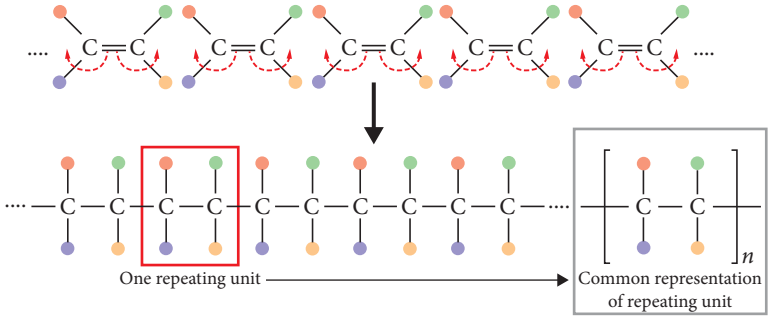


To revise addition reactions of alkenes and alkynes, refer to Chemistry section 6.2, page 285.

Addition polymers form by adding together without the loss of any atoms. They do this through addition polymerisation, which is a type of addition reaction.

For addition polymerisation to occur, the monomer must have a double bond between two carbon atoms. The breaking of the double bond provides each carbon with an available bond to form bonds between the monomers. The number of monomer units that make up these polymers may range from 100 to more than 100 000.

The general process for the formation of addition polymers is shown in Figure C7.4.



◀ **Figure C7.4**
A schematic diagram of the formation of an addition polymer from an alkene

Addition polymers are synthesised through the process of addition polymerisation, which requires a monomer with a double bond. The structure of the monomer determines the structure and properties of the polymer formed

Polymers from ethene (ethylene)

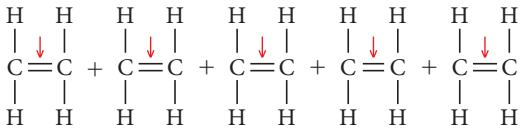
One of the most common addition polymerisation reactions occurs in the production of polyethene, which involves the linking of ethene (ethylene) molecules into long chains. Note that while polyethene is the systematic name for the polymer produced, the IUPAC preferred name is polyethylene. Therefore, the name polyethylene will be used when referring to this polymer.

This is represented by the general equation:

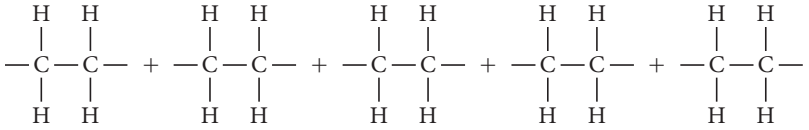
$$n(CH_2{=}CH_2) \rightarrow -CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

During this addition polymerisation, one of the bonds in each of the C=C double bonds is broken, under the influence of a catalyst at high temperature and pressure. This leads to formation of covalent bonds between C atoms on adjacent monomers (ethene molecules) as can be seen below.

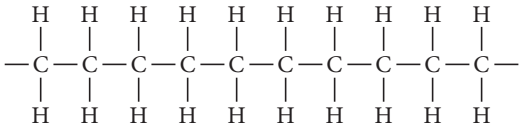
In the presence of a catalyst, one of the bonds in each C=C is broken.



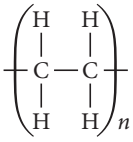
This frees up one electron on each C for further bonding.



New carbon–carbon bonds form between adjacent molecules to give polymer chains.



As can be seen, the polymer is made up of repeating CH_2–CH_2 units, so the structure of the polymer is often written in an abbreviated form $-(-CH_2—CH_2-)-_n$ or:



where n is the number of monomer units in the molecule.

There are two types of polyethylene – low-density polyethylene (LDPE) and high-density polyethylene (HDPE). They are produced by two different processes. Their different properties are a result of differences in their structures.

To see how these properties relate to use, refer to Context 4, 'Polymer chemistry', page 87.

Low-density polyethylene is produced by a gas phase process using high temperature (300°C), high pressure (1000–3000 atm) and an **initiator** (to start the reaction). This product has significant chain branching due to some of the hydrogen atoms being replaced by an alkyl group. The branches prevent the polymer chains packing closely together so there is a lot of space in the product and fewer dispersion forces between them. This leads to its low density, low melting point and greater flexibility.

The Ziegler–Natta process for the production of HDPE uses lower pressures (only a few atmospheres) and temperatures (60°C) and a catalyst that is a mixture of titanium(III) chloride and trialkylaluminium compound (e.g. $(CH_3CH_2)_3Al$). The process forms unbranched polyethylene chains that can pack closely together in an orderly way. Because the chains are packed more closely together, this product has a higher density. There is also stronger bonding because there are more dispersion forces between chains, resulting in higher melting point and less flexibility.

HDPE has a more ordered structure so is said to be more **crystalline**, while LDPE with its more random structure is **amorphous** (non-crystalline). Figure C7.5 shows the difference between the linear chains of HDPE and the branched chains of LDPE.

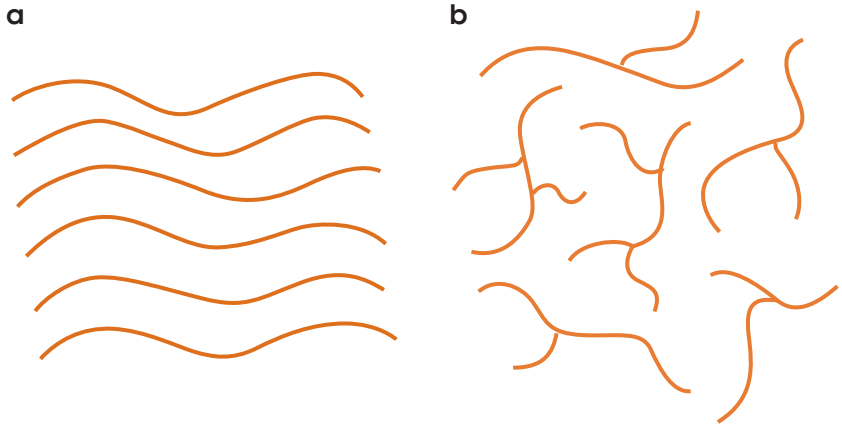


Figure C7.5 ▶ Different arrangements of polymer chains in a) HDPE and b) LDPE

EXPERIMENT 7.1

INVESTIGATING CRYSTALLINE AND AMORPHOUS PACKING OF POLYMER CHAINS

The arrangement of polymer chains and the strength of interactions between adjacent chains is the reason why some plastics are soft and flexible and others are hard and rigid. If the chains can move easily past each other when the plastic is bent, then it will be flexible, but if the chains are held in place, the plastic will be rigid.

When polymer chains are packed closely together in a regular pattern, they form a crystalline area. The more crystalline areas in the polymer there are, the stronger and less flexible it is. The areas where the chains are randomly arranged, and so further apart, are called amorphous.

Many polymers have both crystalline and amorphous regions. Because polymer chains are so long any one chain can be involved in both regions along its length.

Aim

To use spaghetti to make a model of polymer structure

Materials

- Spaghetti (about 100 g)
- Saucepan or large beaker
- Hot plate
- Strainer
- Water
- Transparent container with a flat base and straight sides

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Boiling water can cause serious burns.	Wear protective clothing. Use heatproof gloves to handle the container with boiling water.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Cook the spaghetti according to the manufacturer's instructions.
2. Strain the cooked spaghetti to remove the excess water.
3. Pour the strained spaghetti into the straight-sided container and allow it to cool.
4. Once the spaghetti is cold, turn it out onto a flat surface, being sure it retains its block shape.

Results

Draw a diagram or take a photo of the flat bottom of the spaghetti.



▲ **Figure C7.6** An upturned spaghetti cake

Analysis of results

1. Identify crystalline and amorphous regions on your diagram or photo.
2. Estimate the percentage of crystallinity (that is, how much of your polymer is crystalline) in your 'polymer' and compare this with other students' results.

Discussion

1. Compare how easy it is to lift a piece of spaghetti from an amorphous region and a crystalline region. Discuss this in terms of intermolecular forces.
2. Discuss whether your polymer would be more or less rigid than those of other students. Justify your reasons.

Conclusion

Relate the properties of the amorphous and crystalline regions to the properties of LDPE and HDPE.

WOW

Polyethylene

Shortly after the discovery of polyethylene, World War II began. Within a few years, the production of polyethylene increased dramatically as it became a strategic military material. It was used as electrical insulation for high-frequency radar cables. Production spiralled from 8 grams in 1935 to 1441 tonnes in 1944. Unfortunately, much of the information about the development of polyethylene during this period was lost to view due to its military use.

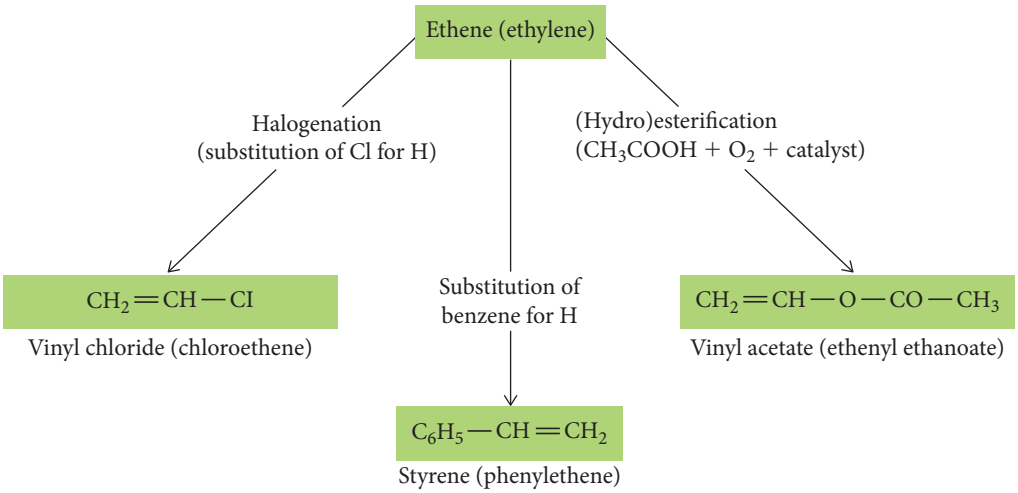
Table C7.1 Differences in structure, properties and uses of LDPE and HDPE

Polymer	Structure and bonding	Properties	Use
Low-density polyethylene (LDPE)	Amorphous (disordered) Branched chains Weak bonding due to fewer dispersion forces between chains that are further apart	Soft, flexible, transparent, impermeable to water vapour, unreactive towards acids and bases, absorbs oils and softens, low melting point (80–95°C), low tensile strength	Plastic bags, toys, plastic food wraps, wire and cable insulation, lamination film for paper and card used in juice and milk cartons, hard disc drives
High-density polyethylene (HDPE)	Crystalline (ordered) Linear chains Stronger bonding due to more dispersion forces and closeness of chains	Denser, tougher, more rigid, higher melting point and greater tensile strength than LDPE, opaque, impermeable to water vapour, unreactive towards acids and bases	Detergent bottles, milk and water jugs, fuel tanks for vehicles, bottle caps, food storage containers, 3D printer filament, plastic surgery

Other addition polymers

As well as being used directly to produce polyethylene, ethene is converted into a range of other useful monomers, which are, in turn, used to produce polymers. This is shown in Figure C7.7.

Figure C7.7 ▶ Monomers produced from ethene

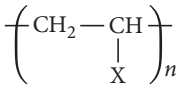


The general reaction for the production of a polymer from an alkene was shown in Figure C7.4, where each coloured circle represented an H or a substituent group. This can also be represented by the general equation:

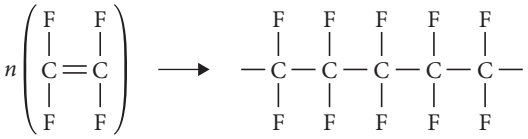
$$n\,(CH_2{=}CH) \longrightarrow -CH_2-CH(X)-CH_2-CH(X)-CH_2-CH(X)-$$

where X may be hydrogen or a substituent group. Substituting the hydrogen with different substituent groups, such as a halogen, benzene or alkyl group, produces polymers with different properties.

As with polyethylene, this can be abbreviated to:



One or more hydrogen atoms of the alkene may be replaced by a different substituent group. A polymer you might be familiar with under its trade name Teflon™ is an example of this. Polytetrafluoroethylene (PTFE) is a polymer formed from the monomer tetrafluoroethylene, which has the formula $—CF_2=CF_2—$. All the hydrogen atoms have been replaced by fluorine atoms. The structure of the resulting polymer is shown below.



To learn more about Teflon, refer to Context 4, 'Polymer chemistry', page 90.

Naming polymers

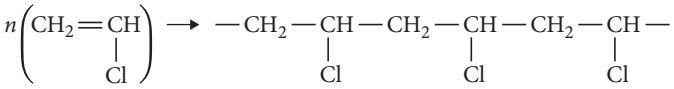
Polymers are named by putting 'poly' in front of the polymer name; for example, polyethylene and polystyrene.

Brackets are used around the name when the monomer name:

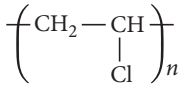
- is more than one word; for example, poly(vinyl chloride)
- begins with a number; for example, poly(1-chloroethene).

Poly(vinyl chloride) (PVC)

Poly(vinyl chloride) (systematic name poly(1-chloroethene)) is made from the monomer vinyl chloride (systematic name chloroethene). Its structure is:



This can be abbreviated to:

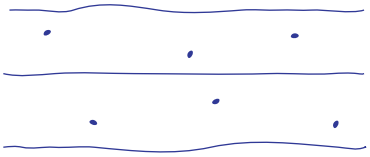


The polymerisation process produces polymer molecules with the chlorine atoms oriented randomly along the chain. The polymer is mainly amorphous (such as LDPE) because of the way the chlorine atoms stick out from the chain and their large size. Although amorphous polymers are usually more flexible than crystalline ones, this is not true for PVC, which tends to be hard and rigid.

Chlorine is a highly electronegative atom so attracts the electrons towards it in the —C—Cl— bond, creating a polar bond with the Cl atoms slightly negative and the C atoms slightly positive. The dipole–dipole interactions add to the dispersion forces between polymer chains to make stronger intermolecular forces, holding the polymer chains more strongly together.

Plasticisers – small molecules inserted between polymer chains – are sometimes added to hold the polymer chains further apart and weaken intermolecular forces between chains. These make the polymer more flexible. The more plasticiser that is added, the more flexible the polymer becomes.

Apart from polyethylene, PVC is the cheapest and most widely used polymer.



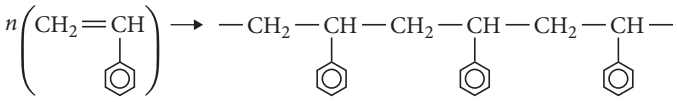
▲ **Figure C7.8** Plasticisers act as spacers forcing the polymer chains further apart

To revise aromatic hydrocarbons, refer to Chemistry section 6.4, page 295.

Polystyrene (PS)

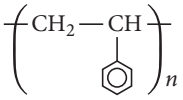
Another common addition polymer is polystyrene. This is made from the monomer styrene (phenylethene), which is an alkene to which the phenyl group ($—C_6H_5$) (a derivative of benzene (C_6H_6)) has been substituted for one of the hydrogens in ethene.

The styrene monomer and a segment of the polystyrene polymer are shown below.



where  = $—C_6H_5$ derived from benzene

This can be abbreviated to:



POLYSTYRENE FOAM

Watch this video to see how polystyrene is turned into polystyrene foam.

Styrene is the common (and IUPAC preferred) name for this monomer. Its systematic name is phenylethene.

Similar to PVC, the polystyrene produces polymer molecules with the phenyl (benzene) ring oriented randomly along the chain. The polymer is mainly amorphous because of the way the rings stick out from the chain and their large size. The symmetry of the phenyl ring means there are no polar bonds, so the only forces acting to hold the chains together are weak dispersion forces. While the large ring groups prevent the polymer chains packing closely together, they also restrict the ability of the chain to flop around so it tends to be clear, hard and brittle. It is readily softened and moulded on heating but becomes rigid when cooled.

WOW

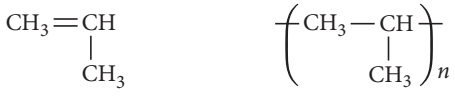
Green styrofoam

The DOW Chemical Company developed a new 'green' process that uses pure carbon dioxide as the blowing agent to produce Styrofoam. This technology eliminated the use of 1600 tonnes of CFC-12 (dichlorodifluoromethane). The CO_2 used in the process is a by-product from existing commercial and natural sources so it does not contribute additional CO_2 to global warming.

Polypropylene (PP)

Polypropylene manufacture uses catalysts, including Ziegler–Natta catalysts. There are three variations of the structure of polypropylene depending on the orientation of the $—CH_3$ alkyl group relative to the chain. The spatial arrangement of these side groups makes a difference to the properties of the polymer.

The structure of propene and the abbreviated form of the polymer is:



Propene Polypropylene

The three possible arrangements are shown in Figure C7.9 where the coloured ovals represent the $—CH_3$ group and the hydrogen atoms have been omitted for simplicity.

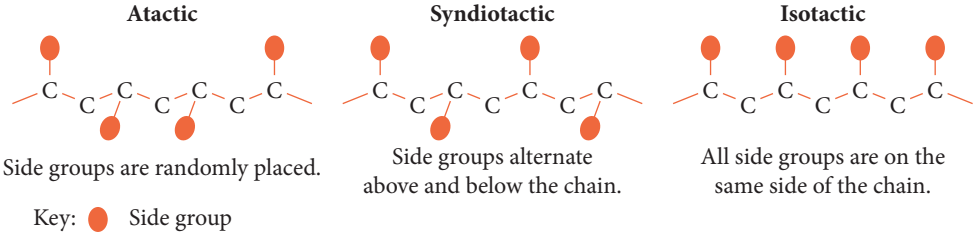


Figure C7.9 ▶ Three possible arrangements of side groups in a linear polymer chain

The regular arrangement of the $-CH_3$ groups on the same side of the polymer chain in the **isotactic** arrangement makes it possible for the chains to pack close together and maximise the dispersion forces between them. This means it is quite strong and hard with excellent resistance to stress, cracking and chemical reactions. It is the common form used to manufacture objects such as crates and ropes.

In the random **atactic** arrangement, the chains cannot lie close together so the forces of attraction are weaker. This results in a softer polymer with a lower melting point. The atactic version formed during the manufacture of the isotactic polymer is considered a waste product and is a soft rubbery polymer, which has limited use mainly as roofing materials and sealants.

Syndiotactic polypropylene has only recently been made on a large scale. In this version, the CH_3 groups alternate above and below the chain. The regularity means the chains can pack closely, resulting in fairly strong intermolecular forces. However, its attractions are not as strong as the isotactic version so it is somewhat softer than the isotactic polymer, but also tough and clear. It is used in packaging and because it is stable to gamma radiation it has applications in medicine such as medical tubing, bags and pouches.

The isotactic and syndiotactic forms of polypropylene are called **stereoregular polymers**. They are semicrystalline. The chains in the crystalline parts are not stretched out in a zig-zag way as in polyethylene, but curl up into regular spirals allowing even stronger bonding.

Table C7.2 summarises information about several common addition polymers.

Table C7.2 Common addition polymers, the monomers they are made from, and some of their uses

Polymer	Name and structure of the monomer	Common uses
Polyethylene	Ethene (ethylene) $CH_2{=}CH_2$	LDPE: milk bottles, soft toys, plastic wrap (cling wrap) HDPE: kitchen utensils and containers, more rigid toys, rubbish bins, tougher carry bags
Polypropylene	Propene (propylene) $CH_2{=}CH{-}CH_3$	Car bumpers, rope and twine, household goods, moulded chairs, carpets
Poly(vinyl chloride) PVC	Vinyl chloride (chloroethene) $CH_2{=}CH{-}Cl$	Electrical insulation, garden hoses, drainage and sewerage pipes, household guttering and downpipes
Polytetrafluoroethylene PTFE (Teflon™)	Tetrafluoroethene $F_2C{=}CF_2$	High-grade electrical insulation, non-stick surfaces on cookware, pipe thread sealant
Polystyrene	Styrene (phenylethene) 	Car battery cases, tool handles, modern furniture, disposable drink cups (both foam and clear), foam packing material
Polyacrylonitrile (acrylics)	Acrylonitrile (cyanoethene) $CH_2{=}CH{-}C{\equiv}N$	As a wool substitute in clothing, blankets, soft furnishings, carpet
Poly(vinyl acetate) PVA	Vinyl acetate (ethenyl ethanoate) $CH_2{=}CH{-}O{-}CO{-}CH_3$	Vinyl coatings on upholstery fabrics, paint, adhesives



To learn more about the use of polymers, refer to Context 4, 'Polymer chemistry', page 88.



To learn more about synthetic rubber, refer to Context 4, 'Polymer chemistry', page 91.

Copolymers

To design new polymers with particular properties, more than one monomer might be used. This mixing of monomers can result in significant changes in the property of a polymer. When polymer chains are built of more than one monomer, the new polymer produced is called a **copolymer**.

A copolymer is a polymer produced from two or more different monomers. The properties of the copolymer are different from those of polymers composed of only one of the individual monomers.

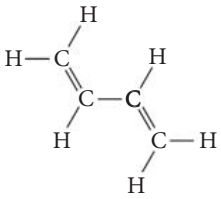


Figure C7.10 ▲
Butadiene monomer

For example, if a butadiene monomer (Figure C7.10) is copolymerised with styrene, the impact strength of the resultant polymer improves considerably and the product can be used to make battery cases and shoe heels. This modified version of polystyrene is called high-impact polystyrene.

Synthetic rubber is the most widely used copolymer. It is a copolymer of styrene and butadiene monomers, which has had further changes made to the polymer chains.

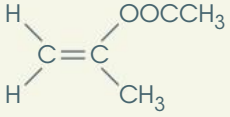
QUESTION SET 7.2

Remembering

1 a Describe what is necessary in a monomer for addition polymerisation to occur.
b Explain the process of addition polymerisation.
2 Name the most common addition monomer and polymer.
3 a What is the difference between an amorphous and a crystalline polymer?
b How and why do these structural differences affect the properties of a polymer?
4 What is a copolymer?

Applying

5 Perspex is made by addition polymerisation from the monomer.



Draw part of the polymer of Perspex (include at least three monomer units).

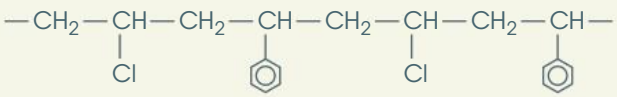
6 Given the polymer:



a write down the structural formula of the repeating unit.
b write down the structural formula of the monomer.
7 a Draw the structures of three possible variations of polystyrene.
b Explain why each of the different structures would have different properties.

8 a Draw the copolymer that would form from equimolar amounts of the monomers ethene and propene.

b Name and draw the structures of the monomers used to make the following polymer.



Analysing

9 Explain why poly(vinyl chloride) forms a hard, rigid polymer yet polystyrene is hard and brittle when they are both amorphous polymers.

10 What is the difference between addition polymerisation and copolymerisation?

7.3 Relating properties, uses and structure

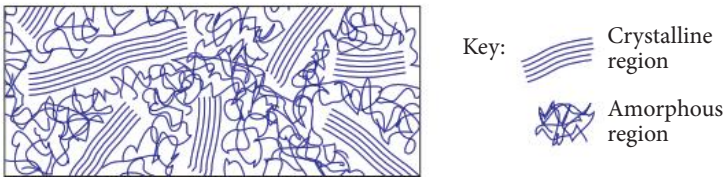
When selecting polymers for particular purposes, it is important to match the properties of the polymer with its intended use. The properties depend on the structure of the polymer molecules and the bonding present.

Important structural features are:

- crystallinity
- branching
- chain length
- side groups
- cross-linking
- stability and biodegradability.

Crystallinity

Molecules of linear polymers such as polyethylene can flex and twist. As a result, some molecules will be tangled. The final polymer will have regions that are crystalline and regions that are amorphous (which you saw in the spaghetti cake simulation).



◀ **Figure C7.11** Crystalline and amorphous regions in a polymer

In crystalline regions, the polymer chains are closer together so the intermolecular bonding is stronger. This leads to greater rigidity and higher softening and melting points. Other properties that arise when the chains are closer are greater density, opaque appearance and resistance to air, moisture and chemicals. Crystalline regions are non-permeable.

In amorphous regions, the chains are tangled, disordered and have no definite structure. The large gaps between chains means the intermolecular forces are weaker. This leads to more flexibility and lower softening and melting points. Other related properties include transparency, permeability to water, air and chemicals and lower density.

The degree of crystallinity in a polymer determines the properties related to that factor. In commercial polymer production the percentage of crystalline and amorphous regions can be controlled. Therefore, manufacturers can control many of the properties of the resulting polymer.

Branching

Chains with little or no branching can pack together more closely than chains with a high degree of branching. Therefore, polymers with low chain branching will tend to be more crystalline, so denser, less transparent and less flexible than polymers with a high degree of chain branching, which tend to be more amorphous.

The formation of highly branched structures requires more extreme reaction conditions because covalent bonds have to be broken to insert a branch.

To see how different side groups are used to manipulate products, refer to Context 4, 'Polymer chemistry', page 97.

Chain length

Chain length is controlled by the conditions and proportions of chemicals used in the polymerisation process. In any batch of polymer, there will be chains of different lengths so average molecular weight is considered as this reflects the number of monomer units that combine to make one polymer molecule.

For a given type of polymer, the longer the chain length and the smaller the differences in chain length, the higher is the melting point and the harder the polymer.

Chain length affects the flow characteristics of the softened polymer, which in turn affects manufacturing processes. Long chains make the softened polymer more viscous and difficult to extrude, whereas chains that are too short mean the extruded product will sag as it exits the machine. Also, short chains cannot withstand moulding processes that involve blowing the polymer into shape using gases at high temperature.

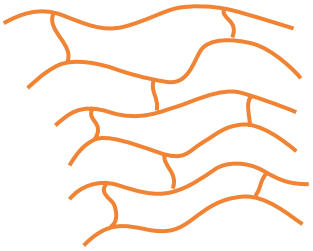


Figure C7.12 ▲
Cross-linking joins chains to each other.

Side groups

Another way to change the properties of a polymer is to change the side groups that are attached to the carbon backbone. Putting a bigger side group into a linear chain reduces the flexibility of the polymer, making it stiffer. For example, replacing a hydrogen in polyethylene with a chlorine atom (PVC) or a benzene ring (polystyrene) restricts the ability of the chain to flop around and causes the material to become stiffer and more rigid.

Cross-linking

The rigidity and hardness of a polymer can be increased by **cross-linking**. In this process, linear chains are linked together to form a more rigid two- or three-dimensional structure. These cross-links usually form strong covalent or ionic bonds between the polymer chains. The greater the amount of cross-linking, the more strongly the polymer chains are bonded and the more rigid the polymer. Figure C7.12 shows an example of cross-linking.

For example, if natural rubber is heated with some sulfur, S–S bonds form between adjacent chains. This makes the material harder and more elastic. This process is called **vulcanisation**.

CROSS-LINKING

Visit this website for more information about expanded polystyrene foam.

EXPERIMENT 7.2

MAKING A CROSS-LINKED POLYMER

PVA glue is made of long chains of poly(vinyl alcohol), which slide past each other fairly easily, allowing the glue to be poured from the bottle. When borax is mixed with the PVA glue, borate ions ($B(OH)_4^-$) form bonds between the polymer molecules of the PVA. The resultant 'slime' is an example of a cross-linked polymer.

Aim

To make slime and test its properties

Materials

- 50 mL of poly(vinyl alcohol)
- 10–15 mL of 4% solution of borax (4 g sodium borate (borax) in 96 mL water)
- Distilled water
- Disposable plastic cup

- 10 mL measuring cylinder
- Wooden paddle pop stick
- Gloves
- Newspaper

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Borax and PVA will burn eyes.	Wear a laboratory coat and safety glasses and wash your hands at the end of the experiment. Keep your hands away from your eyes while using the chemicals.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Cover your work area with a few layers of newspaper.
2. Place 50 mL of PVA glue in a plastic cup and add 50 mL of water. Mix thoroughly.
3. Slowly add the borax solution, approximately 5 mL at a time, stirring thoroughly with a wooden paddle pop stick upon each addition. Be careful not to add too much borax or the slime will become too stiff.
4. Remove the slime with the wooden stick and work it with your hands until it is no longer sticky.
5. Testing properties
   - **a** Take some of the slime in one hand and stretch it slowly. Repeat the stretching exercise rapidly. Does it break apart easier when pulled quickly or slowly?
   - **b** Place the slime in a ball on the table and poke it quickly with your finger. Poke it again slowly. What happens?
   - **c** Form the slime into a ball and see if it bounces.
   - **d** Place a ball of slime on the table and observe it for a few minutes. Does it flow into a puddle or maintain its shape? Does this demonstrate that the slime is a liquid or a solid?
   - **e** Press the slime down on a piece of newspaper. Is the image transferred to the slime?
   - **f** Write on a piece of paper with a permanent marker and then with a water-based marker. Press the slime down on the writing. Is the image transferred to the slime?
   - **g** Try to make slime bubbles by wrapping the slime around the end of a straw and blowing gently. An airtight seal must be made between the straw and the slime.
   - **h** Place a small amount of slime on a paper towel and set it aside to dry until the following lesson. Note any differences in its appearance and properties.

Results

Record your observations and results of the property tests.

Analysis of results

Describe how cross-linking has changed the properties of PVA.

Discussion

1. **a** Write the formula for the monomer of PVA.
   b Draw a structural diagram of a section of a PVA polymer (including at least four repeating units).
2. Draw a diagram to show how the borax forms cross-links between the polymer chains. Use information at the weblink to help draw your diagram.
3. How does water affect the elasticity of the polymer?

POLYMERS

Visit this website for more information about polymers.

Stability and biodegradability

Most of the bonds in polymers are strong covalent C—C and C—H bonds, so the polymers are fairly stable. This means that most synthetic polymers, unlike natural polymers, are not biodegradable.

However, PVC has C—Cl bonds, which are weaker than C—H bonds, and are broken by ultraviolet light. The polymer becomes brittle and cracked if it has been in sunlight for some time. Special additives, called stabilisers, are added to the polymer to protect it from degradation.

To increase the biodegradability of synthetic polymers, chemists have copolymerised them with natural polymer segments, such as those in starch. This causes the polymer chain to break down into many smaller segments.

STRUCTURE, PROPERTIES AND USES

Watch this video to find out more about plastics and polymer films.

INVESTIGATION 7.1

IDENTIFYING PLASTICS BY THEIR DENSITY

Plastics are synthetic materials with a wide range of properties. One property that can be used to help identify plastics is their density.

You are to design an experiment to identify unknown samples and also to separate and identify the pieces in the mixture.

What is your aim?

Write an aim for your investigation.

What will you need?

The following information will help you.

- The densities ($g\,mL^{-1}$) of common plastics are: HDPE 0.95–0.97; LDPE 0.917–0.940; PETE 1.38–1.39; PP 0.90–0.91; PS (in solid form) 1.04–1.05; PS (in foam form) variable but always less than 1; and PVC (rigid) 1.30–1.58; PVC (flexible) 1.16–1.35.
- The densities of nine different solutions are:

Liquid	Density ($g\,mL^{-1}$)
Methanol	0.79
52% ethanol/water mixture	0.911
38% ethanol/water mixture	0.9408
24% ethanol/water mixture	0.9549
Water	1.00
10% solution of NaCl	1.08
Saturated solution of $MgCl_2$	1.34
40% $CaCl_2$ solution	1.398
Saturated solution of $ZnCl_2$	2.01

What are the risks?

Construct a table similar to the one below. Identify specific risks involved in the investigation and ways that you will manage the risks to avoid injuries or damage to equipment. Check the relevant MSDS.

What are the risks in doing this investigation?	How can you manage these risks to stay safe?
Methanol and ethanol are highly flammable.	

How will you carry out your investigation?

1 Consider how you will verify the densities of known samples before testing unknown samples.

2 Take care that no air bubbles adhere to the samples, and shake the tube to check that samples are actually floating.

What results will you collect?

Would a data table be the best way to record your results?

How will you analyse your results?

Identify the unknown samples, giving reasons for your decisions.

What have you found?

1 Decide which polymer would be best used for each of the following and why.
   - **a** As a replacement for the lead sinkers used in fishing
   - **b** To make a toy boat

2 Were any plastics difficult to distinguish? What other properties could be used to separate these plastics?

POLYMERS

Watch this video to revise polymers and their properties.

QUESTION SET 7.3

Remembering

1 Explain how the percentage of crystalline regions and amorphous regions in a polymer affect its properties.
2 What is cross-linking and how does it change the properties of a polymer?

Understanding

3 Explain the relationship between crystallinity and branching.
4 Suggest explanations why:
   - **a** polymers with larger side groups are stiffer.
   - **b** polymers with longer chains form more viscous liquids.

Applying

5 Suggest why cross-linked polymers are not recycled.
6 List four properties that would make a polymer suitable for use as a:
   - **a** disposable juice bottle.
   - **b** bag in which a roast can be cooked in the oven.
   - **c** transparent cover for outdoor light bulbs.
   - **d** tubes for a drip in a hospital.
   - **e** plastic raincoat.

7.4 Condensation polymers

Addition polymerisation requires that the monomer have a double bond. However, if organic molecules have a functional group at each end, a functional group can undergo a condensation reaction with a functional group on another molecule to form a **condensation polymer**.

Functional groups such as $—NH_2$, —OH, —COOH and —COCl are suitable for condensation polymerisation.

Condensation polymers are formed when two monomer molecules join together to eliminate as small molecule (often water). The process is called condensation polymerisation.

Polyesters and polyamides (nylons) are examples of synthetic condensation polymers whereas polysaccharides (cellulose and starch) and proteins are examples of natural condensation polymers.

Polyesters

To revise ester formation, refer to Chemistry section 6.9, page 311.

Polyesters are condensation polymers in which the monomers are joined by an ester link. Recall from Chemistry section 6.9 that an ester and water are formed when a carboxylic acid reacts with an alcohol.

To form a polyester, the monomer molecules need to join at each end, which means they need to have either a carboxylic acid or an alcohol functional group at each end.

Polyesters can be produced from:

- a single monomer that has a hydroxyl (—OH) functional group at one end and a carboxyl (—COOH) functional group at the other
- two different monomers – one monomer with hydroxyl groups at each end (a **diol**) and one monomer with carboxyl functional groups at each end (a **dicarboxylic acid**)

The general production of a polyester from a single monomer is shown in Figure C7.13. The monomers must be aligned so the hydroxyl and carboxyl acid groups are next to each other.

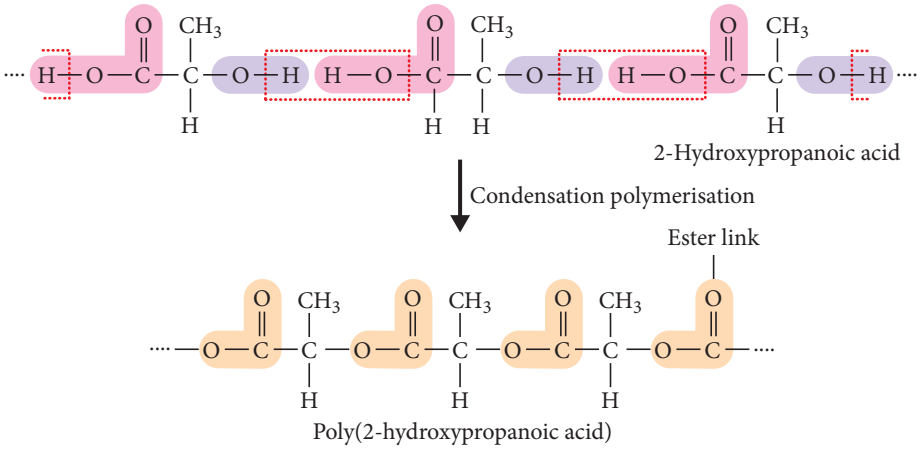
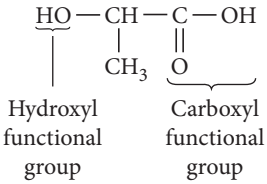
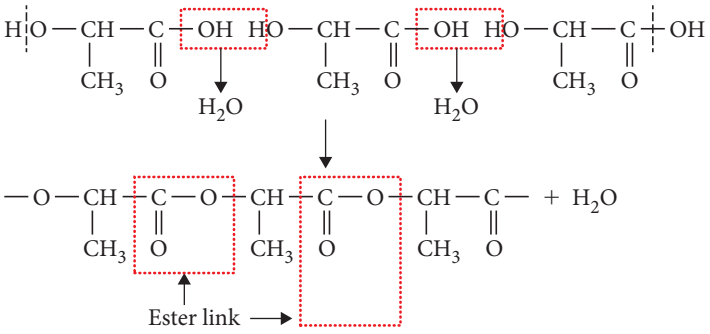


Figure C7.13 ▶ The formation of a polyester from a single monomer

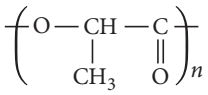
An example of a polyester is poly(lactic acid), which is used to make biodegradable surgical sutures. Lactic acid (2-hydroxypropanoic acid) has a hydroxyl (—OH) functional group at one end and a carboxyl (—COOH) functional group at the other. The structure is:



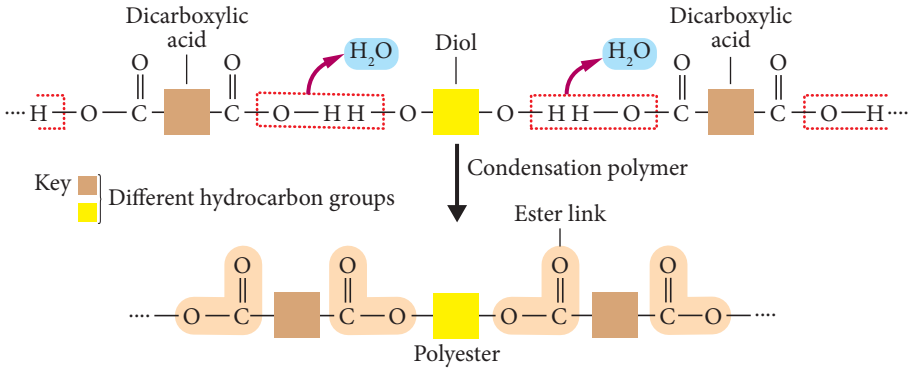
The molecules are able to polymerise through an esterification reaction between the carboxyl group of one molecule and the hydroxyl group of another, as shown below.



The general formula for the polymer is:



The production of a polyester from two different monomers (a diol and a dicarboxylic acid) is shown in Figure C7.14. The monomers must be aligned so a hydroxyl group is next to a carboxyl group. Because this polymer is made from more than one monomer, it is classified as a copolymer.



◀ **Figure C7.14**
The formation of a polyester from a diol monomer and a dicarboxylic monomer



To learn about uses of polyesters, refer to Context 4, 'Polymer chemistry', page 96.

The first practically useful and the most widely used polyester is PET. This polyester has become the world's most rapidly growing textile fibre with manufacturers producing very fine microfibres for use in sportswear and other clothing items.

The two monomers used to make PET are ethylene glycol (ethane-1,2-diol) and terephthalic acid (benzene-1,4-dicarboxylic acid). Their structures are:



Ethylene glycol

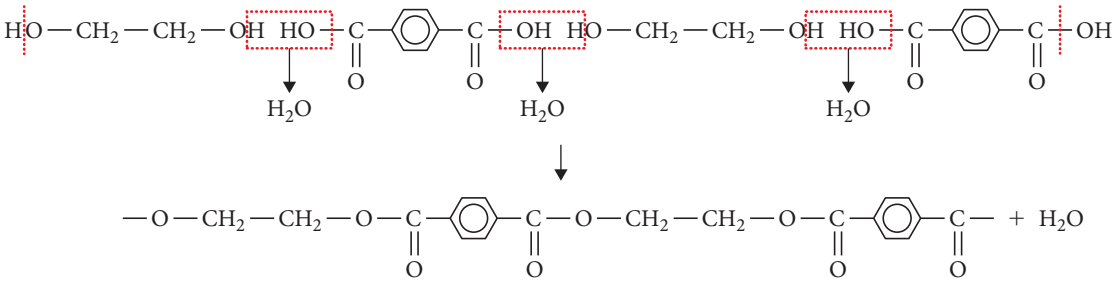
Terephthalic acid



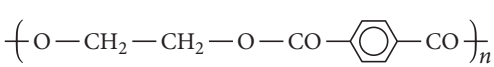
POLYESTERS

Visit this website to find out more about polyesters and how they are manufactured.

The two monomers esterify as shown below.



The abbreviated form of the repeating unit is:





To revise hydrolysis of esters, refer to Chemistry section 6.9, page 312.

One disadvantage of polyester is that it is easily damaged by acids and alkalis. This results in the ester linkages being hydrolysed back to the acid and alcohol monomers. This means that polyester fabrics will end up with holes if an acid or alkali is spilt on them.

Polyamides

Polyamides are condensation polymers in which the repeating units are held together by **amide links** (—CO—NH—). This link is also found in proteins where it is called a peptide link.

One of the most important classes of natural polyamides is proteins. The most commonly known synthetic polyamide is nylon. Nylon duplicates some of the properties of natural polyamides and has a wide variety of uses, including fibres to make fabrics, machine components and domestic appliances.

There are various types of nylon depending on the monomers used in its preparation. The first nylon to be produced was nylon-6,6 while the simplest is nylon-6. These two nylons account for about 80 per cent of all nylon manufacture, of which 25 per cent is used for fibre applications.

To revise amines and amides, refer to Chemistry section 6.10, page 316.

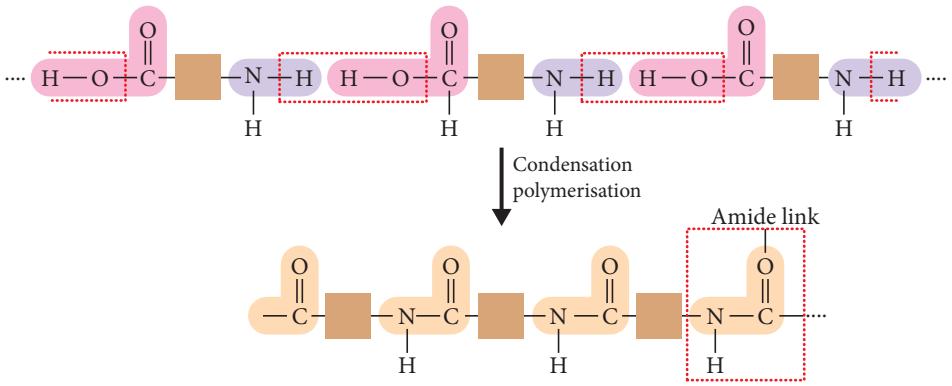
As with polyesters, the monomer molecules must join at each end, which means they need to have either a carboxylic acid or amino functional group at each end.

They can be produced from:

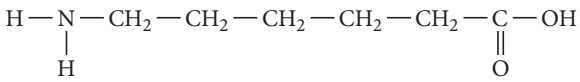
- a single monomer that has an amino ($—NH_2$) functional group at one end and a carboxyl (—COOH) functional group at the other
- two different monomers – one monomer with amino functional groups at each end (a **diamine**) and one monomer with carboxyl functional groups at each end (a dicarboxylic acid).

The general production of a polyamide from a single monomer is shown in Figure C7.15. The monomers must be aligned so the amino and carboxyl acid groups are next to each other.

Figure C7.15 ▶ The formation of a polyamide from a single monomer

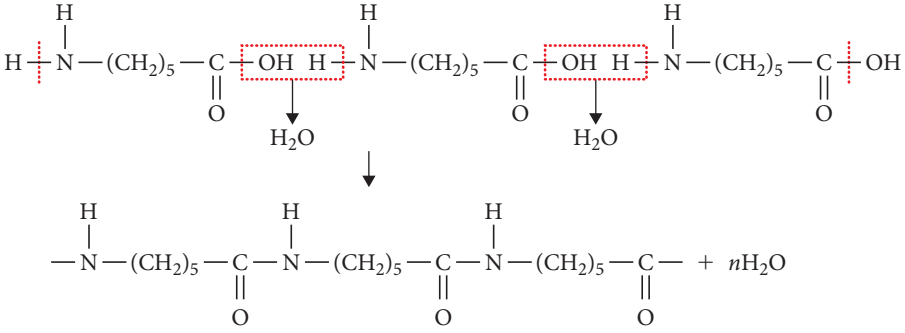


For example, nylon-6 is made from 6-aminohexanoic acid, which has the structure:

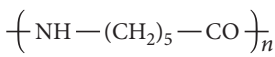


This structure can be abbreviated to $H_2N—(CH_2)_5—COOH$.

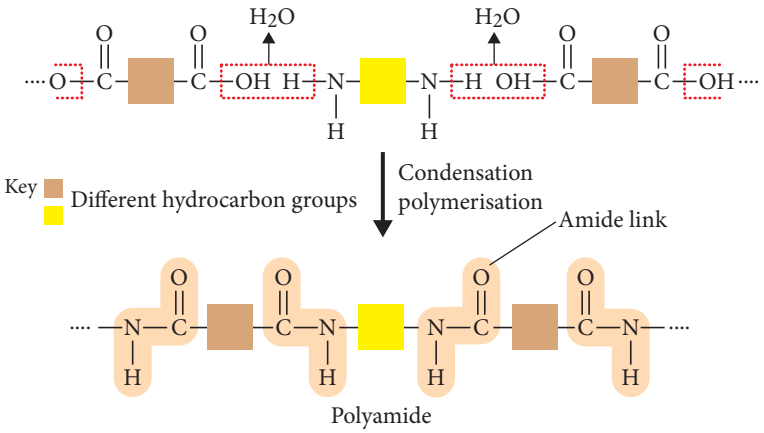
The molecules polymerise through a condensation reaction between the carboxyl group on one molecule and the amino group on another:



The general structure of this polyamide is:

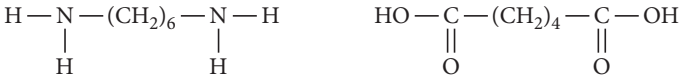


The production of a polyamide from two different monomers (a diamine and a dicarboxylic acid) is shown in Figure C7.16. The monomers must be aligned so that an amino group is next to a carboxyl group. Because this polymer is made of more than one monomer it is classified as a copolymer.



◀ **Figure C7.16**
The formation of a polyamide from different monomers

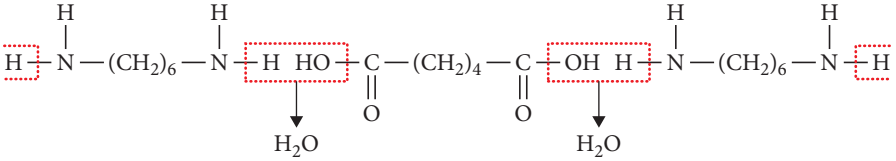
Nylon-6,6 is made from monomers that each have six carbon atoms. The two monomers are 1,6-diaminohexane (also called hexamethylene diamine) and hexanedioic acid (also called adipic acid). The structures of each of these monomers is:

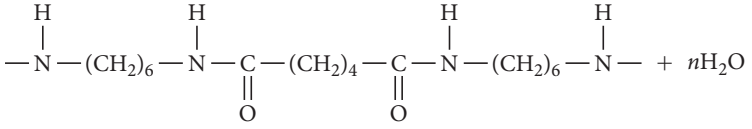


1,6-Diaminohexane

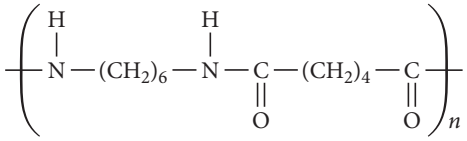
Hexanedioic acid

The two monomers react to product the polyester:





Its structure can be abbreviated to:



Naming nylons

The naming of nylons reflects the number of carbon atoms in the monomers used to make them. Nylons are named by giving the number(s) of carbon atoms in the monomer(s) as a suffix. If there are two monomers, the number for the diamine comes first.

INVENTION OF NYLON

Watch this video about how nylon was invented.

To learn more about polyamides, refer to Context 4, 'Polymer chemistry', page 99.

MANUFACTURE OF NYLON

Visit this website for information about nylons.

Nylon-6 is made from one monomer containing six carbon atoms with an amino group at one end and a carboxyl group at the other.

Different nylons have different properties. The longer the chains of —CH_2— groups. the lower the nylon's melting temperature and the less it absorbs water.

Nylon-6,6 is made from two different monomers, making it a copolymer. It is made from a diamine monomer containing six carbon atoms and a dicarboxylic acid containing six carbon atoms.

QUESTION SET 7.4

Remembering

1 Name two types of condensation polymers.

2 Explain how condensation polymerisation is different from addition polymerisation.

3 Draw the structure of an:

- **a** ester linkage.
- **b** amide link.

Applying

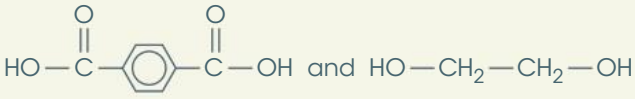
4 **a** Draw a segment of the structure of:

- **i** poly(glycolic acid) formed from the monomer HO—CH_2—COOH.
- **ii** nylon-5 formed from the monomer H_2N—CH_2—CH_2—CH_2—CH_2—COOH.

b Draw the abbreviated structures for the segments in parts **a i** and **ii**.

5 Draw three repeat segments showing the structure of the polymers formed when the following react.

a



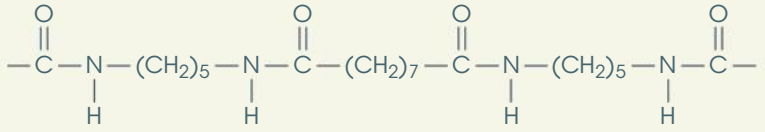
b $H_2N—(CH_2)_4—NH_2$ and $HOOC—CH_2—CH_2—COOH$

6 For each of the polymers in Question **5**:

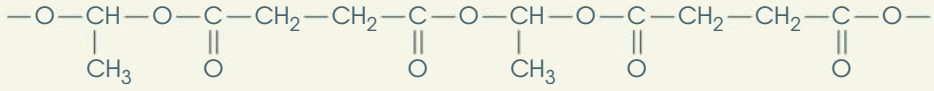
- **a** identify the type of polymer.
- **b** circle and name the type of link present.
- **c** name the functional groups present in the monomers.

7 For each of the polymers **i** and **ii**:

i



ii



- **a** identify the type of polymer.
- **b** draw the structure of the monomers.
- **c** identify the organic group to which the monomer belongs.
- **d** name the monomers.

Analysing

8 For each of the polymers shown in Question **7**, predict the type of bonding that would occur between polymer chains and explain why.

7.5 Carbohydrates

Carbohydrates, which include simple sugars, are natural polymers. They are the most widely distributed and abundant compounds in the biosphere. The carbohydrate, cellulose, the main component of plants, is probably the most abundant organic compound on Earth. Cellulose is a polymer found in the cell walls of plants. It is responsible for giving plants their structural strength. Cellulose is indigestible to humans but is part of the fibre needed in a balanced diet.

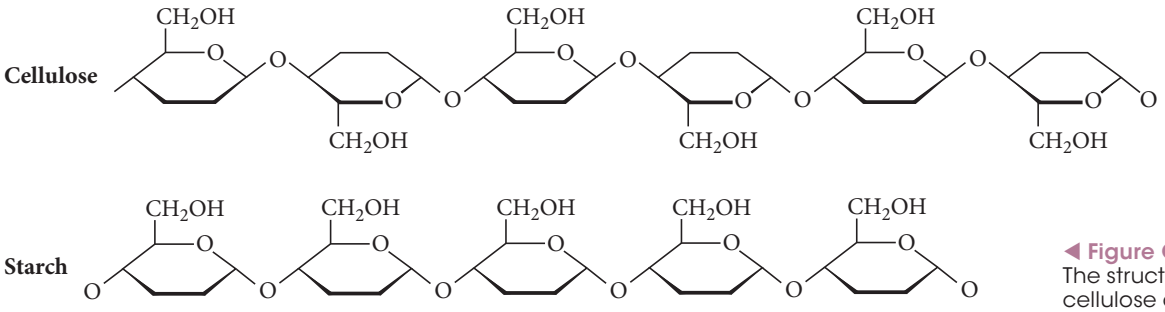
Starch is also a carbohydrate, but it can be digested by humans and is as an important nutrient, providing a source of biochemical energy for the biological processes that occur in our body.

Both cellulose and starch are made of the same monomer, glucose, but they have different properties. The difference is in the structure. In starch, the oxygen atom joining the pair of monomers is pointing downwards while in cellulose the oxygen atom is pointing upwards then downwards. This appears to be the only difference between the two polymers but it changes the properties dramatically.

▼ **Figure C7.17**
Cellulose is found in the cell walls of plant cells.



NataliTerr/Shutterstock.com



◀ **Figure C7.18**
The structures of cellulose and starch

The structure of carbohydrates determines their properties.

Structures of carbohydrates

Carbohydrates are a diverse group of molecules but they are all made up of the same three elements – carbon, hydrogen and oxygen – and there are always twice as many hydrogen atoms as there are oxygen atoms. The most common formula for carbohydrates is $C_6H_{12}O_6$. Carbohydrates (carbon + hydrate) are named because their formula can be written as $C_x(H_2O)_y$. The structures of carbohydrates feature a ring containing carbon atoms (usually four to six) and one oxygen atom. The carbons of the ring are bonded to —OH groups and H atoms. Two or more rings may be joined together to make bigger molecules. The —OH groups participate in hydrogen bonds, which makes starch and sugar soluble in water.

Complex carbohydrates such as cellulose and starch are polymers made from simple units (sugars) called **monosaccharides**, meaning single (one) sugar, that are joined through a condensation polymerisation reaction.

Monosaccharides

Monosaccharides are commonly referred to as simple sugars. They are all isomers of $C_6H_{12}O_6$. Glucose, fructose and galactose have different structures and properties as shown in Figure C7.19.

The thick wedge-shaped bonds in the ring indicate that the plane of the ring is perpendicular to the paper. The H atoms and —OH and —CH_2OH groups attached to the ring are above and below that plane. The positioning of these groups is important because it determines which compound the structure represents. Glucose and galactose differ only in the location of one —OH group, yet they have noticeably different properties.

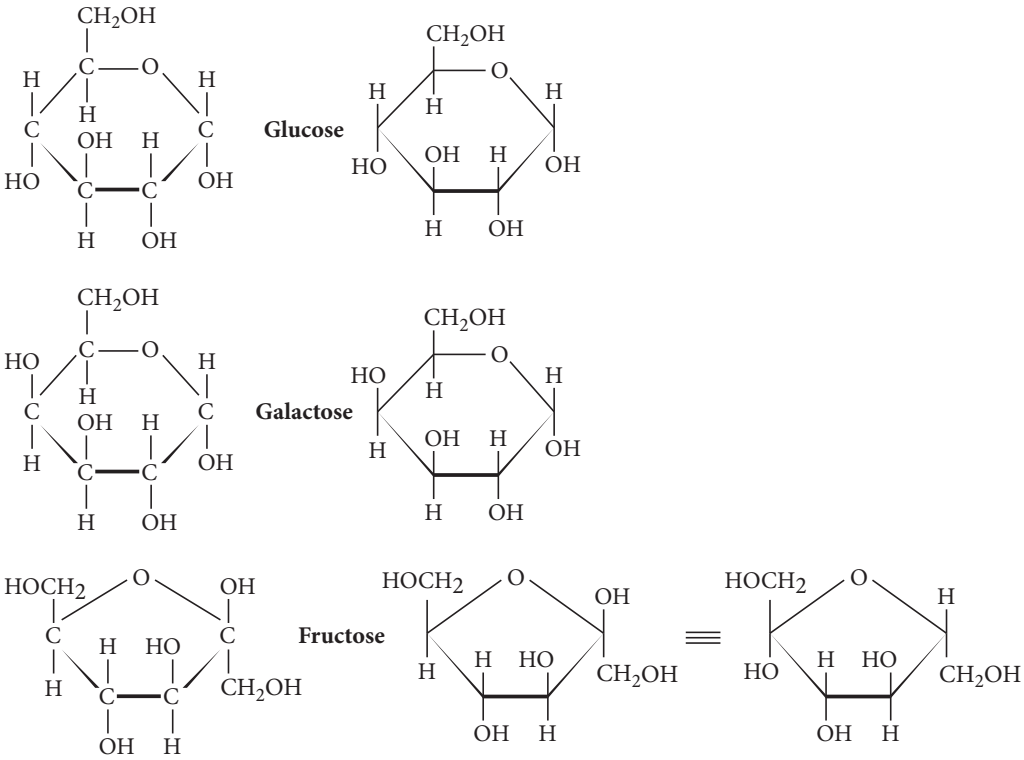
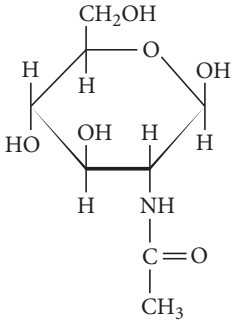


Figure C7.19 ▶ Structures of three common monosaccharides. The left-hand structures show all the atoms of the molecules; in the right-hand ones, the carbon atoms are not labelled. The right-hand structure for fructose is just the middle structure flipped through 180°.

WOW

Chitin

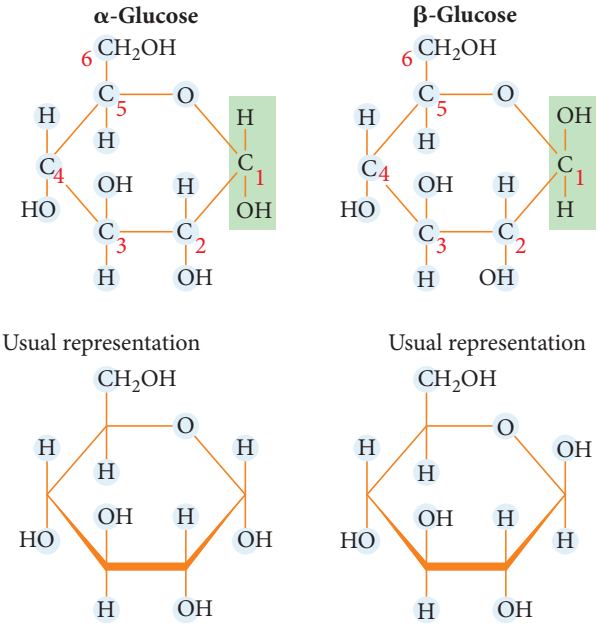
Chitin is a structural carbohydrate that makes up the protective exoskeleton of arthropods such as beetles and lobsters. The monomer in chitin is similar to glucose but it has a side chain containing an amide group attached to one carbon in the ring.



Chitin monomer

They are all white crystalline, sweet-tasting compounds. Of the three, glucose is the most important in human nutrition because sugar in this form is used by our bodies as an energy source.

There are two isomers of glucose called α-glucose and β-glucose. These are shown in Figure C7.20. The α form of glucose has the OH group on C1 below the plane of the ring whereas in β-glucose it is above the plane of the ring.



▲ **Figure C7.20** The α and β forms of glucose

Disaccharides

Monosaccharides are the building blocks of other carbohydrates. When two monosaccharides join, they form a **disaccharide**. Common disaccharides are sucrose from cane sugar, maltose from malt and lactose from milk.

The reaction that occurs to form the disaccharide is a condensation reaction because a water molecule is released. This can be written simply as:

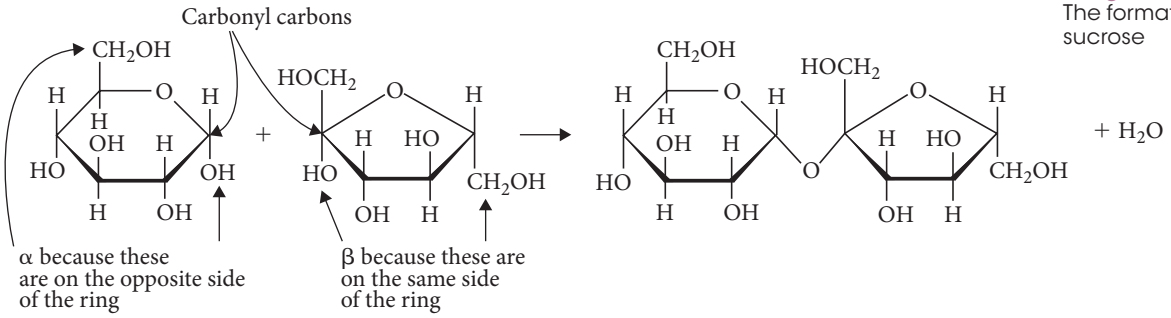
$$2C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O$$

While the molecular formula makes the reaction seem simple, when the structural formulas are considered the situation becomes more complicated because there are different isomers and different forms of these isomers.

Sucrose is formed by linking the carbonyl carbons of α-glucose and β-fructose.

To see the sugars that are in wine, refer to Context 1, 'Wine' page 9.

α-glucose + β-fructose ⟶ sucrose + water



◀ **Figure C7.21**
The formation of sucrose

The link that joins the monosaccharides is called a **glycosidic link**, —C—O—C—.

Maltose is produced when two glucose monomers join and lactose is produced when a glucose monomer and a galactose monomer join.

These three disaccharides have different properties due to their different structures. Maltose and galactose are not as sweet as sucrose while fructose is sweeter than sucrose. Their melting points are: lactose 253°C, sucrose 186°C and maltose 160°C. They have similar densities.

Disaccharides are too large to pass through cell membranes so they need to be broken down to their constituent monomers in the digestive system. This hydrolysis reaction is the reverse of the condensation polymerisation reaction by which they are formed and adds water to give a new —OH group to the fructose ring and —H to the oxygen on the glucose ring.

DEHYDRATED SUGAR

Watch this video showing what happens when sugar is dehydrated.

EXPERIMENT 7.3

ANALYSING SUGAR IN SOFT DRINKS

We have become more conscious of the number of kilojoules (or calories) in food and drinks. The kilojoules in soft drinks are due to a sugar. A broad range of drinks is marketed according to their sugar content or lack of sugar; for example, Coke Zero, Pepsi Max.

Sugar also increases the density of a solution. You may have already performed some investigations related to density of solutions if you studied Context 1, 'Wine', page 5. The density of solutions of unknown sugar concentration can compared with the densities of sugar solutions of known concentration.

Aim

Write an aim for your experiment.

Materials

- 60g sugar
- 6 × 100mL beakers
- Distilled water

- 10 mL pipette
- Pipette filler
- Electronic balance
- Drinks to test, such as Coca-Cola™, Pepsi™, diet soft drink, apple juice, a sports drink, Lucozade

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
The samples could become contaminated.	Do not consume any of the drinks being tested.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Prepare 100 mL of each of five standard sugar solutions of (% weight/weight) 0%, 5%, 10%, 15% and 20%. For example, a 5% solution can be made by dissolving 5 g of sugar in 95 g of water.
2. Weigh an empty beaker.
3. Use the pipette to add exactly 10 mL of the 0% sugar solution to the empty beaker and reweigh it.
4. Record the masses in a data table.
5. Repeat steps 2–4 with each of the prepared solutions. Make sure you rinse the pipette and remove any trapped liquid between each use.
6. Calculate the density of each of the standard solutions.
7. Repeat steps 2–4 with each of the drinks provided. Note: carbonated drinks must be allowed to go flat before performing any measurements.

Results

Draw up a results table similar to the following.

Sugar solution or drink	Mass of empty beaker (g)	Mass of beaker with solution (g)	Mass of solution (g)	Volume of solution (mL)	Density ($g\,mL^{-1}$)
0%					
5%					
10%					
15%					
20%					

Analysis of results

1. On a piece of graph paper, plot a graph of density versus sugar content (%) and draw the line of best fit.
2. Use the graph to determine the sugar content of each of the drinks you tested.

Discussion

1. **a** Why did you need the carbonated drinks to go flat before conducting the test?
   b If this had not been done, what effect would it have had on the values obtained?
2. What value did you obtain for the diet drink? What did you expect? Comment on any difference.
3. The sugar found in most drinks is usually fructose; however, you used sucrose to make the standard solutions. Use a chemical data book to find out the densities of fructose and sucrose. Comment on what assumption was made about the densities in this experiment and how this impacted on the results.

Conclusion

Summarise what you have found.

Polysaccharides

Polysaccharides are often called complex carbohydrates. They are formed when a large number (hundreds to thousands) of monosaccharides join through condensation polymerisation. A polysaccharide may contain only one type or monomer or different types. This gives the carbohydrate its primary structure.

Many polysaccharides form stable secondary structures due to bonding within or between polysaccharide chains to form helices or chain-linked sheets. However, these secondary structures can often be disrupted by temperature increases, changing pH or adding a denaturing agent.

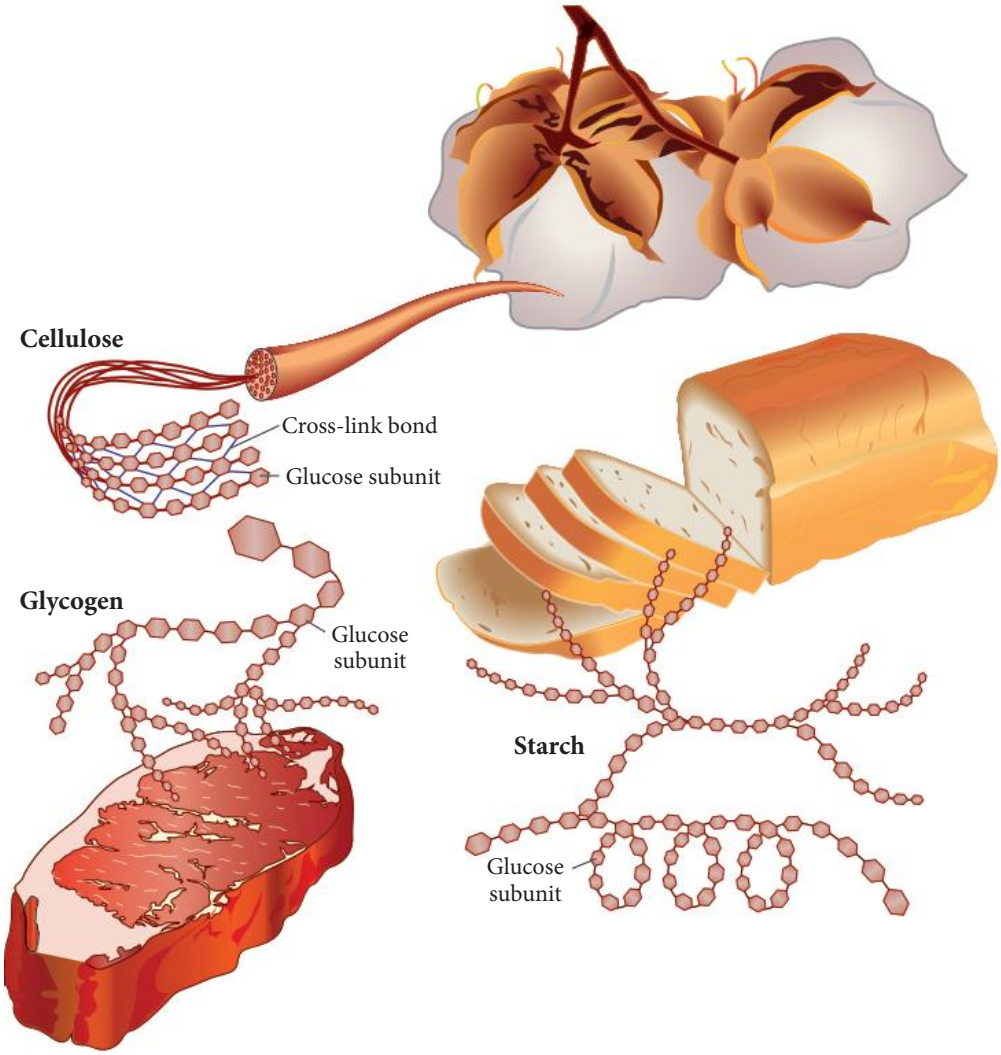
The three most important polysaccharides are starch and cellulose from plants and glycogen from animals. These polysaccharides are all polymers of glucose but have different glycosidic links, amount of branching of the polymer chain and degree of polymerisation.

The nature of the glycosidic linkage is different because cellulose consists of long chains of β-glucose joined together (Figure C7.18) while starch and glycogen consist of α-glucose molecules joined together (Figure C7.18).

The starch polymer consists of two parts. The smaller part (about 20%), amylose, is a straight-chain polymer that can form spirals due to intrachain hydrogen bonding. Amylopectin, which forms the major part (80%), is a highly branched chain. These chains occur when one glucose molecule condenses with three other glucose molecules instead of the normal two. This part of the molecule cannot form spirals.

Cellulose has unbranched molecules that preferentially form hydrogen bonds with each other to form a strong cross-linked type structure. This cross-linking gives cellulose its strength and rigidity. Unlike starch, cellulose is insoluble in water. Cellulose is a highly crystalline polysaccharide, which accounts many of its properties.

Glycogen is highly branched with an amorphous structure.



◀ **Figure C7.22**
Starch, cellulose and glycogen

To learn about how cellulose is used, refer to Context 4, 'Polymer chemistry', page 102.

Sports drinks contain high concentrations (4–8%) of sugar to provide energy to athletes, but the more concentrated the sugar, the longer it takes to leave the stomach and enter the small intestine. Because carbohydrate absorption depends on intestinal transport proteins and there are different transporters for different sugars, scientists are working to optimise different combinations of carbohydrates in sports drink formulations.

CARBOHYDRATES

Visit this website to find out more about carbohydrates.

QUESTION SET 7.5

Remembering

1 Describe the differences between monosaccharides, disaccharides and polysaccharides.
2 Name and draw the structure of the linkage that joins monomer units together.
3 What functional group is characteristic of carbohydrates?

Understanding

4 Explain why monosaccharides and disaccharides are soluble in water.
5 a Why is the combined mass of the monosaccharides resulting from the hydrolysis of a disaccharide greater than that of the disaccharide?
  b Write the equation for the hydrolysis of sucrose.
6 Describe the differences between cellulose, starch and glycogen in terms of their structure, bonding and properties.

Analysing

7 Using the empirical formula for starch, $C_6H_{10}O_5$:
  a calculate the percentage of oxygen and carbon in one repeating unit.
  b calculate the molecular weight of a molecule of starch that contained 300 monomer units.
  c write an equation for the hydrolysis of one unit.
  d write an equation for the hydrolysis of 50 units.
  e explain whether or not the equation is accurate and why.

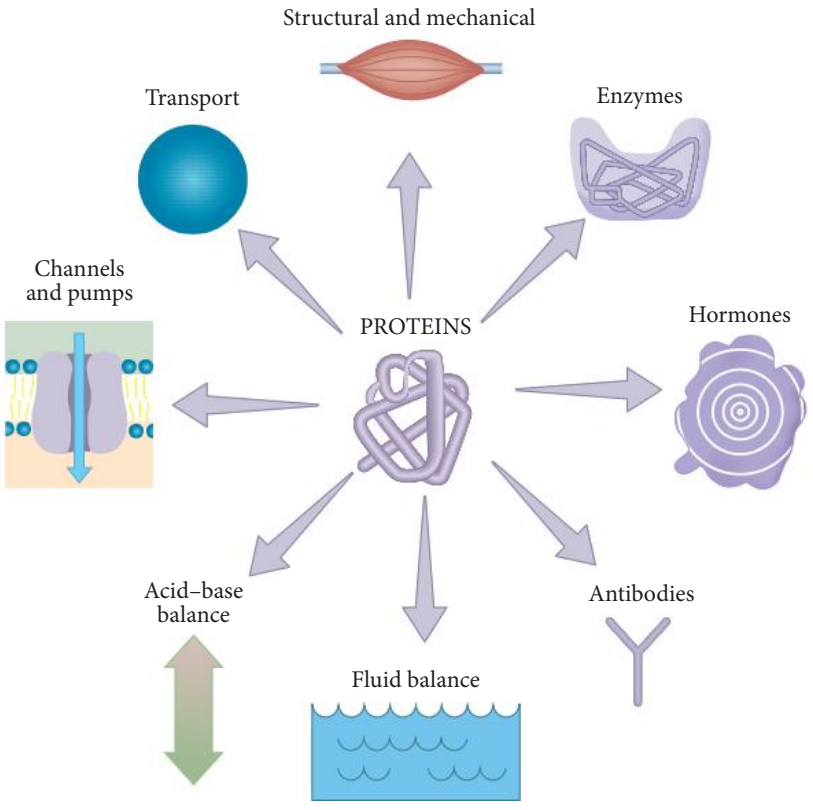


Figure C7.23 ▲ Protein functions

7.6 Proteins

Proteins are an essential part of every living cell. They are the major structural component of hair, skin and muscle so structural and mechanical proteins are tough, insoluble in water and have a stringy appearance. Proteins are also essential to the chemical processes that take place in our bodies, including transporting oxygen (haemoglobin), nutrients and minerals through the bloodstream. Many hormones, such as insulin, are proteins and all enzymes (biological catalysts) and antibodies are proteins.

Proteins are large polymers (polyamides or polypeptides) formed when many smaller monomer molecules link together in a condensation polymerisation reaction. The monomer building blocks of proteins are amino acids. Although there are only 20 different amino acids found in proteins, there are hundreds of thousands of different proteins.

All protein molecules are long chain-like molecules with different side groups strung out along a repeating backbone of mainly carbon atoms. The long protein chains are normally folded into complex and highly specific shapes, allowing them to perform very specialised functions within living organisms.

WOW

Proteins

The word 'protein' derives from the Greek *protos*, meaning 'first'. They were given this name when they were discovered in the 19th century because they were believed to be the chemical essence of life. We now know that life depends on the interaction of thousands of chemicals. Proteins are only one group of these. Nevertheless, proteins make up about half of the body's non-water mass.

The most important features of a protein that enable it to perform its specific biological function include the:

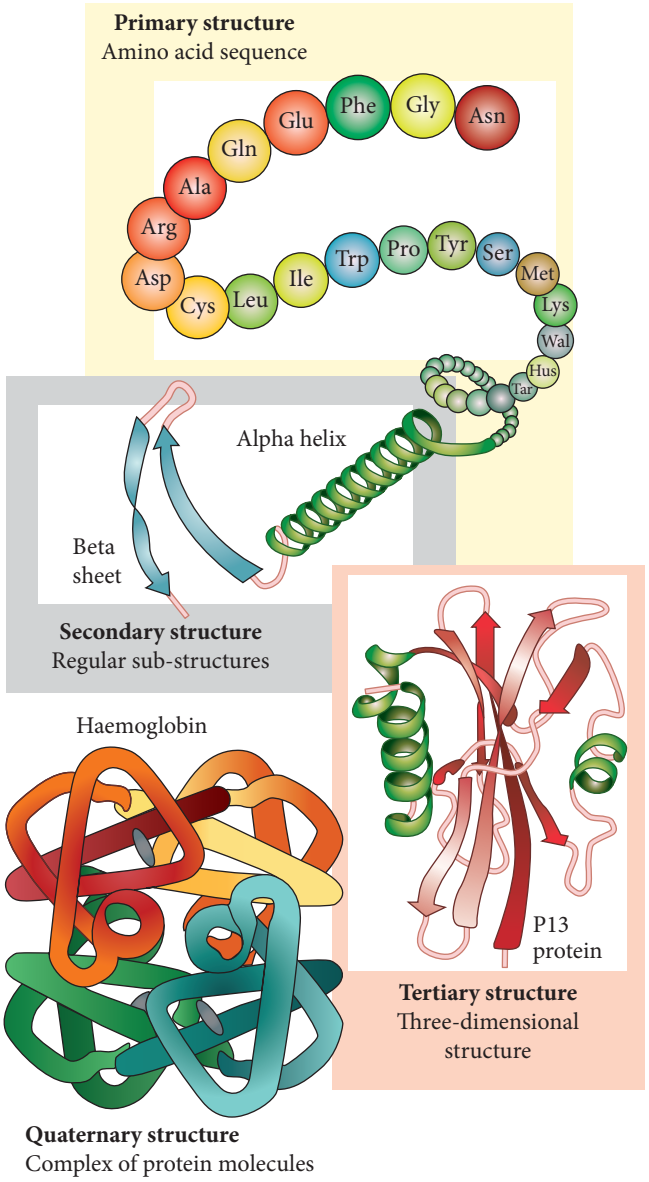
- nature and sequence of amino acids that make up the polymer chain and give the primary structure
- way the polymer chain is arranged within segments to give it its secondary structure
- way the secondary structure is arranged to give the whole molecule its tertiary, and sometimes quaternary, structure.

STRUCTURE AND FUNCTION OF PROTEINS

Watch the video about proteins.

The primary, secondary, tertiary, and sometimes quaternary, structures of proteins determine their properties and biological functions.

▼ Figure C7.24
Levels of protein structure



Primary structure

The sequence of amino acids determines the primary structure of a protein chain. The way the protein folds to produce the secondary structure depends on this sequence.

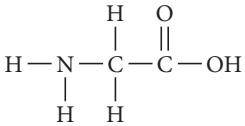
Amino acids contain the amino ($—NH_2$) functional group and the carboxyl (—COOH) functional group. This means amino acids have both acidic and basic properties.

The monomer $H_2N—(CH_2)_5—COOH$ used to make nylon-6 has an amino and an acid functional group but is not classified as an amino acid because amino acids have two specific structural features that are not present in this molecule.

The special structural features common to the 20 amino acid monomers that form proteins are:

- the amino and carboxyl functional groups are attached to the same carbon atom (called the **alpha-carbon**)
- a hydrogen attached to the alpha-carbon.

The simplest amino acid is glycine, which has the structure:



These monomers are **alpha-amino acids** because they can only form proteins when the two functional groups are joined to the same carbon atom. The general structure of an alpha-amino acid is shown in Figure C7.25.

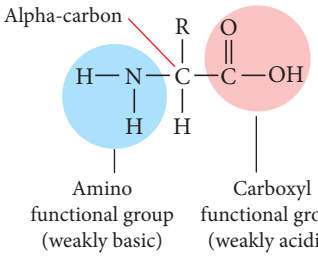


Figure C7.25 ▶ General structure of an alpha amino acid

The 'R' group is a carbon-containing side chain. The 20 amino acids commonly found in proteins can be categorised into three broad groups. They are amino acids with:

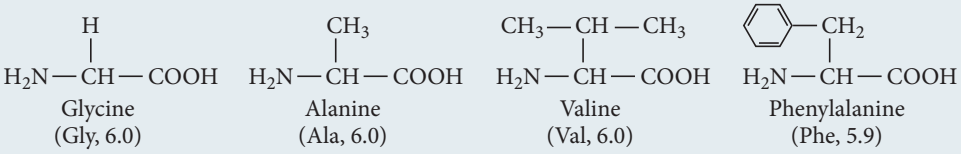
a non-polar R groups

b polar R groups capable of forming ions (generally with an additional $—NH_2$ or —COOH groups as part of the R chain)

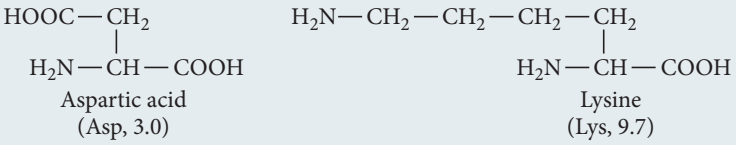
c polar R groups that generally do not form ions (generally with an —OH or —SH group as part of the R chain) (Figure C7.26).

When drawing an alpha-amino acid, the amino group is always written on the left and the carboxyl group is always written on the right.

a With non-polar groups



b With polar R groups that form ions



c Polar R groups that do not generally form ions

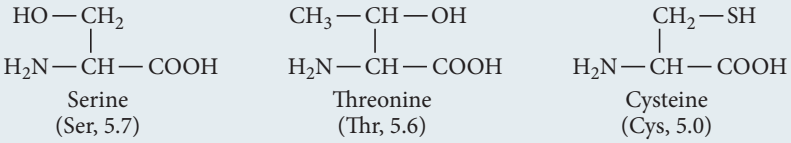
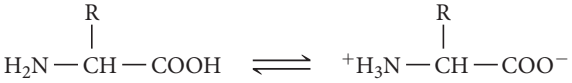


Figure C7.26 ▶ Common amino acids found in proteins. Their usual abbreviations are given in brackets along with their isoelectric points (the pH at which they exist as the neutral molecule).

Forming zwitterions

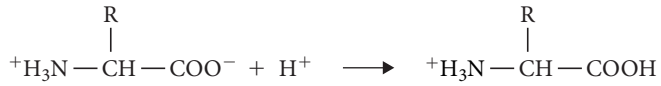
The amino acids shown in Figure C7.26 have been written as neutral molecules. However, the acidic –COOH group tends to lose a proton to form $-COO^-$, while the basic amine group $-NH_2$ tends to gain a proton to form $-NH_3^+$. This results in a dipolar ion called a **zwitterion**. Therefore, in aqueous solution, amino acids exist as an equilibrium mixture of neutral molecules with the dipolar ion:



The dipolar structure means amino acids exhibit some of the properties of ionic substances – they form crystalline solids, have relatively high melting points and are soluble in water.

Recall that the $-COOH$ group is a weak acid and $-NH_2$ is a weak base. This means the pH of a solution containing the amino acid affects the nature of the zwitterion.

In strongly acidic solutions (e.g. pH 2–3), the $-COO^-$ group gains a proton to become $-COOH$ while the $-NH_3^+$ does not change. So the zwitterion changes to a cation below:



In alkaline solutions, the $-NH_3^+$ group loses a proton while the $-COO^-$ group does not change. So the zwitterion changes to an anion:



The pH at which an amino acid exists as an overall neutral zwitterion is called the **isoelectric point**. This is different for different amino acids because of the influence of the different R groups. At pH values less than the isoelectric point, the zwitterion will exist as the cation; and at pH values higher than the isoelectric point, the zwitterion will exist as the anion.

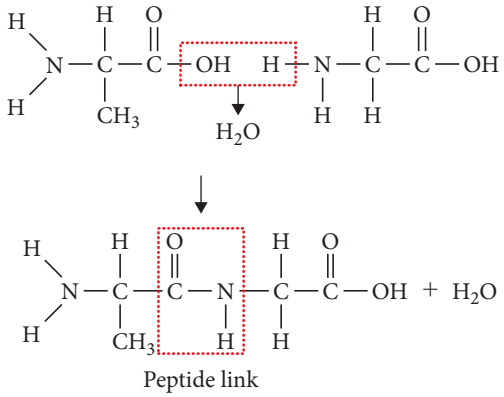
Joining amino acids

Amino acids undergo condensation polymerisation to form an amide in the same way as nylon on page 346. The bonds that hold amino acids together are covalent bonds.



To revise polyamides, refer to Chemistry section 7.4, page 346.

The link that joins two amino acids together is called a **peptide link** (and is the same as the amide link in polyamides). The compound formed when two amino acids join together is called a **dipeptide** and when long chains of amino acid units join, the result is a **polypeptide**. For example, when glycine reacts with alanine, the result is the alanylglycine dipeptide:



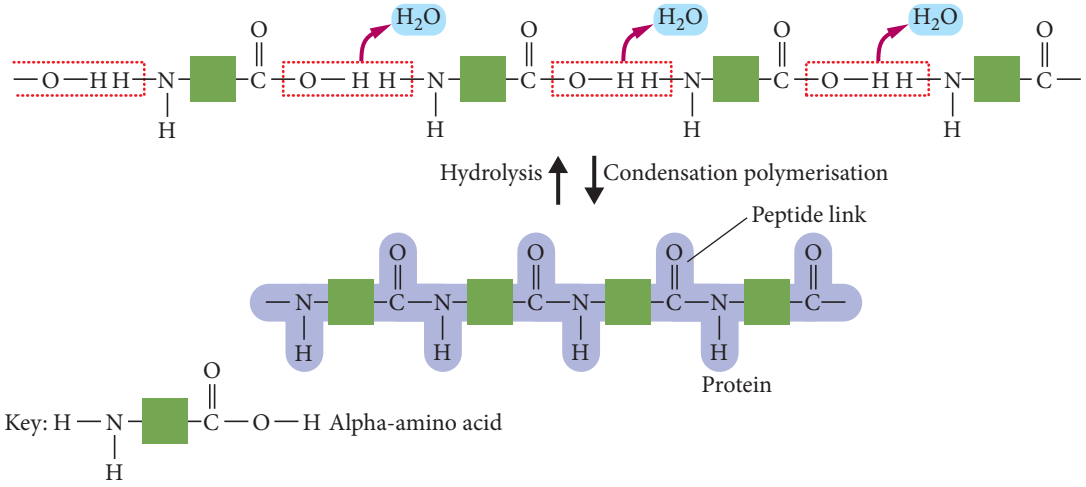
Peptide link

The resultant dipeptide has functional groups at each end so it can continue to react with other amino acids to produce a polypeptide as shown in Figure C7.27.

Unlike nylons, which have a regular repeating unit, polypeptides can have various combinations of amino acids. Biochemists have developed a shorthand way of drawing them. Each of the 20 amino acids that make up the body's proteins has been given a three-letter abbreviation, as can be seen in the examples in Figure C7.26. The dipeptide alanylglycine, shown above, can be written as Ala–Gly. A possible sequence of a peptide with eight amino acids is Lys–Cys–Asp–Cys–Gly–Val–Val–Thr.

When hundreds to thousands of amino acid units join together, the result is a protein. So proteins are giant polypeptides. In the final protein, there is still an amino group at one end and a carboxyl group at the other.

Figure C7.27 ▶ Forming a polypeptide and breaking it down again



In humans and other animals, proteins are broken down (hydrolysed) during digestion into their constituent amino acids. This process is brought about by enzymes (which are themselves proteins), some of which will only break the peptide link between specific amino acids.

In the laboratory, proteins can be broken down by warming them with some strong hydrochloric acid but the breakages are non-specific.

Secondary structure

The secondary structure is the way individual amino acids in the protein chain bond to other amino acids in the same or adjacent chains. The secondary structure of a protein involves folding or twisting as a result of hydrogen bonding. The arrangement is determined mainly by hydrogen bonding between non-bonding electron pairs on the oxygen of the C=O group of one amino acid and a hydrogen atom attached to the amine group of another amino acid.

There are two common arrangements of the protein chain:

- When the —C=O group of one amino acid forms a hydrogen bond to an —NH group four peptide links further along the chain, the result is a spiral structure called an α-helix.
- When stretched regions of different chains lie alongside each other, hydrogen bonding may occur between chains, resulting in a β-pleated sheet structure.

These two different secondary structures are shown in Figure C7.28. The nature of the secondary structure of a protein is an important determinant of its functional properties. Factors such as heat, pH and the presence of salts can affect the hydrogen bonding and the stability of the secondary structure.

Tertiary and quaternary structure

The most important level of organisation is the tertiary structure of a protein (the overall three-dimensional shape). This is the way the helices and sheets of the secondary structure fold up and interact together into a three-dimensional structure.

The overall tertiary shape may be long and narrow, which is typical of the fibrous proteins such as keratin (skin, wool, feathers) and collagen (tendons, cartilage and hides), or a roughly spherical globular shape, which is typical of insulin, haemoglobin and enzymes.

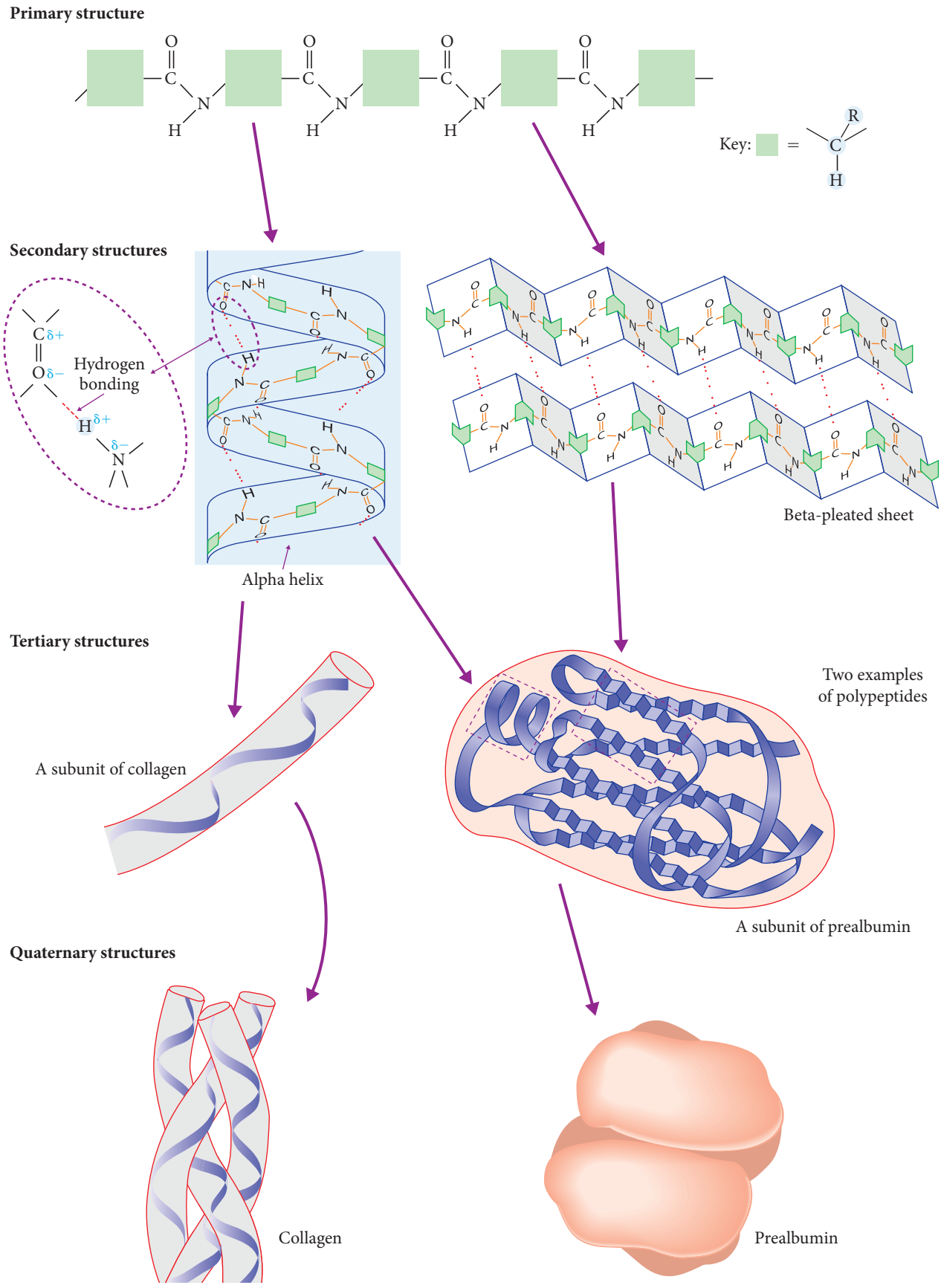
There are five types of interactions in determining the tertiary structure. These are due to interactions between the R group side chains on the amino acids that make up the chain. These are:

- dispersion forces between non-polar side chains on amino acids such as phenylalanine and valine
- hydrogen bonding between polar side groups such as —C=O and —OH or —N—N on amino acids such as serine and asparagine, as well as hydrogen bonding between peptide groups
- ionic attraction between ionisable side chains such as $—COO^-$ in aspartic acid and $—NH_3^+$ in lysine
- dipole–dipole attraction between polar side groups such as serine and threonine
- covalent bonding formed when the —SH groups on the side chain of cysteine are oxidised to form –S–S– (disulfide) links (a form of cross-linking between chains); cysteine plays a special role in providing greater stability to many tertiary structures.

Examples of each of these links are shown in Figure C7.29.

BUILD A PROTEIN

Visit the website to obtain instructions and a template to build a model of a protein.



▲ **Figure C7.28**
The structure of proteins

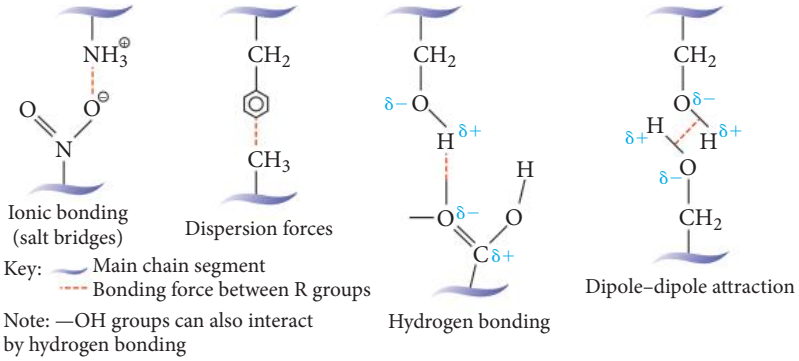


Figure C7.29 ▶ Examples of the intermolecular forces that determine the tertiary structure of a protein

WORLDWIDE PDB

The Worldwide Protein Data Bank (PDB) houses an international repository of structural data of proteins. The information is accessed and contributed to by scientists worldwide.

If there is more than one polypeptide chain involved, then there may be a quaternary structure. The three-dimensional tertiary or quaternary structure of the overall protein is what allows it to interact with other molecules. For example, an enzyme must have a three-dimensional structure that allows it to interact specifically with its substrate; and haemoglobin (made of four polypeptide subunits) must have the correct three-dimensional structure so it can interact with iron and oxygen. Or a protein that sits on DNA to turn genes on or off has a three-dimensional structure that enables it to find exactly which spot to go to.

QUESTION SET 7.6

Remembering

1 Draw and name the link that occurs between amino acid monomers.

2 **a** Draw the general structure of an amino acid and label the two functional groups of this molecule.

b Redraw the general structure from part **a** to show a zwitterion.

3 What are the three broad groups into which amino acids can be categorised?

4 Describe three levels of organisation of a protein and the relationship between levels.

Understanding

5 Explain the different types of bonding that occur in the tertiary structure of a protein and categorise them from strongest to weakest.

6 What is the difference between an amide link and a peptide link?

7 Draw the structural formula of a dipeptide formed between the following amino acids and identify the link between them.

a Alanine and cysteine

b Glycine and serine

8 For each of the amino acids listed draw the structural formula of the zwitterion form of the molecule.

a Valine

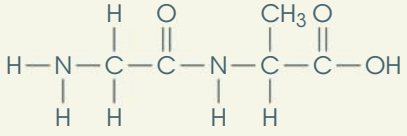
b Lysine

c Serine

Applying

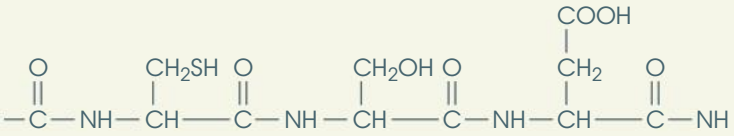
9 Write the equation for the hydrolysis of the dipeptides shown below and name the amino acids formed.

a



b $H_2N-CH(CH_3-CH-CH_3)-CO-NH-CH(CH_2-SH)-COOH$

10 A section of a protein chain is shown.



a How many different amino acids reacted to produce this segment?

b Draw the structure of the amino acids identified in part **a**.

c Explain the difference between this segment of a protein molecule and a segment of nylon-6.

REVISION

Visit this website to revise polymers and ethanol then take a test to check your understanding.

Reflecting

11 Predict what would happen to the secondary and tertiary structures of a protein if amino acids with polar groups were replaced with ones with non-polar groups.

CHAPTER CHECKLIST

You should know:

- the relationship between polymer and monomer
- the characteristics of addition and condensation polymerisation
- the differences between thermosetting and thermoplastic polymers
- the process by which addition polymers form
- the factors that influence the properties of a polymer
- how different structures of the same polymer affect its properties
- the processes by which condensation polymers form
- the linkages in polyesters and polyamides
- how amino acids bond to form proteins
- the difference between and effect of primary, secondary and tertiary structures in proteins.

You should be able to:

- identify and name polymers and monomers from their structures
- draw structures of monomers and polymers
- predict the properties of a polymer based on its structure
- relate structure and properties and bonding in a polymer
- identify the reactants and products of particular synthesis reactions
- identify the main functional groups in monomers and predict the structure of the polymer that would form from these
- distinguish between a polyester and a polyamine
- identify the different units in carbohydrates
- relate the properties of different carbohydrates to their structure
- identify the bonding in proteins at different levels of structure.

CHAPTER GLOSSARY

addition polymer a polymer that forms by molecules adding together without the loss of any atoms

alpha-amino acid an amino acid in which the amine and carboxyl functional groups are attached to the same carbon atom; proteins can only form from alpha-amino acids

alpha-carbon the carbon atom of an amino acid to which is attached the amino and carboxyl functional groups, a hydrogen and a side chain

amide link the functional group produced by the condensation reaction between a $—NH_2$ functional group and a —COOH functional group

amorphous substances that do not have an extended ordered arrangement of molecules

atactic the random arrangement of side groups on both sides of a polymer chain

carbohydrate a family of natural compounds made up of carbon, hydrogen and oxygen, many of which conform to the general formula $C_x(H_2O)_y$

catalytic cracking the process in which high molecular weight (high boiling point) fractions from crude oil are broken into lower molecular weight (lower boiling point) substances

condensation polymer a polymer that forms by the elimination of a small molecule (often water) when monomers join together

copolymer a polymer consisting of two or more different monomers

cross-linking the process by which two or more polymer chains are joined together to form an extended two-dimensional network

crystalline a substance with an ordered arrangement of atoms, ions or molecules in the solid

diamine a molecule that has two amino ($—NH_2$) functional groups

dicarboxylic acid a molecule that has two carboxyl (—COOH) functional groups

diol an alcohol molecule that has two hydroxyl (—OH) functional groups

dipeptide a molecule formed by the joining of two amino acids in a condensation reaction by a peptide link

disaccharide a carbohydrate such as sucrose, maltose and lactose, formed by a condensation reaction to join by a glycosidic link between two monosaccharides

enzyme a protein that catalyses chemical reactions in living organisms by orienting molecules in the correct manner and lowering the activation energy

glycosidic link the —C—O—C— group that is produced when two monosaccharides join

initiator a chemical species that reacts with a monomer to form an intermediate compound which enables the linking of monomers to form a polymer; it is incorporated into the polymer so is not a catalyst

isoelectric point the pH at which an amino acid exists as an overall neutral zwitterion

isotactic the orderly arrangement of side groups on the same side of a polymer chain

monomer a small molecule that combines with other monomers to make a polymer

monosaccharide the simplest carbohydrate molecule that is a monomer of sugar and polysaccharides; commonly exists as a five- or six-membered ring with hydroxyl groups attached

peptide link the functional group produced by the condensation reaction between a $—NH_2$ functional group and a —COOH functional group of different amino acids

plastic a material that is capable of being moulded by heat and pressure

plasticiser a small molecule inserted between polymer chains to hold them further apart

polyamide a polymer formed by a condensation polymerisation reaction between an amine group ($—NH_2$) and a carboxylic acid group (—COOH)

polyester a polymer formed by a condensation polymerisation reaction between an alcohol group (—OH) and a carboxylic acid group (—COOH)

polymer a substance consisting of long macromolecular chains

polymerisation a chemical reaction in which many small molecules combine to form one large molecule

polypeptide a long chain of amino acids that folds into secondary and tertiary protein shapes through the use of intermolecular forces

polysaccharide a high molecular mass condensation polymer such as starch and cellulose, made from monosaccharides

protein a high molecular mass copolymer resulting from condensation polymerisation reactions between amino acids

stereoregular polymer a polymer with an ordered arrangement of side groups along the carbon backbone

syndiotactic the alternating arrangement of side groups on each side of a polymer chain

thermoplastic a polymer that can be melted and reshaped

thermosetting a polymer that cannot be melted and reformed

vulcanisation the process of strengthening a material such as rubber by combining it with sulfur and other additives and then applying heat and pressure

zeolite an inorganic compound of aluminium, silicon and oxygen with metal ions, used for cracking alkanes into shorter chains

zwitterion an ion that has a positive and a negative charge on the same group of atoms; can be formed from compounds that contain both acidic and basic groups in their molecules, such as amino acids

CHAPTER REVIEW QUESTIONS

Remembering

1 Describe the similarities and differences between addition and condensation polymerisation.
2 Describe the differences between isotactic, atactic and syndiotactic versions of a polymer and relate these to the properties of the polymer.
3 Explain how and why the following factors affect the property of a polymer.
   a Cross-linking
   b Branching
   c Side groups
4 A linear polymer is one in which:
   A the chains are aligned parallel to each other.
   B there is no cross-linking.
   C there are many side branches.
   D the chains are very short.
5 As the chain length of a polymer increases, the polymer becomes:
   A stronger.
   B less dense.
   C more easily melted.
   D more soluble.
6 For a monomer to be able to undergo addition polymerisation, it should contain:
   A at least three carbon atoms.
   B both hydrogen and oxygen.
   C a multiple bond.
   D a halogen.
7 When a polymer is formed by condensation polymerisation, the:
   A mass of the polymer formed is less than the total mass of reactants.
   B polymer must be linear.
   C polymer must be cross-linked.
   D polymer must be thermoplastic.
8 When sucrose is digested, it yields the two monosaccharides:
   A glucose and lactose.
   B glucose and maltose.
   C glucose and glucose.
   D glucose and fructose.
9 Which of the following compounds is an amino acid?
   A Ethanoic acid
   B Alanine
   C Lactose
   D DNA
10 Which of the following is *not* a property of most amino acids?
   A They are highly soluble in non-polar organic solvents.
   B They may be positively and/or negatively charged.
   C They may act as both acids and bases.
   D They can undergo condensation polymerisation forming polypeptides.
11 What are the similarities and differences between an ester link, an amide link and a peptide link?

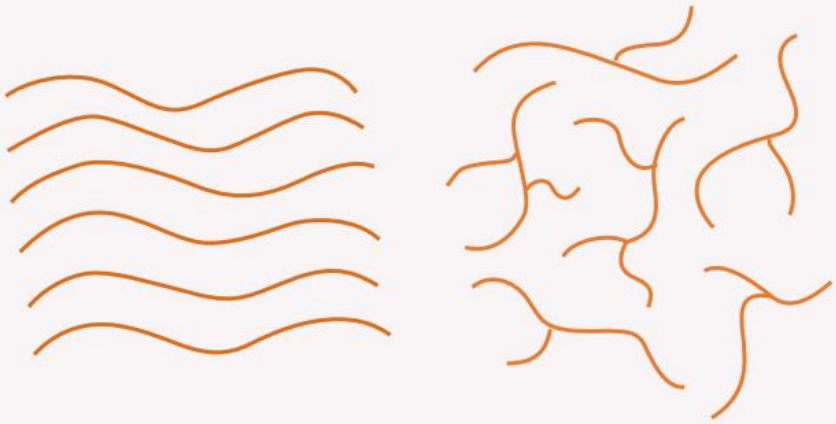
12 Name three monosaccharides, three disaccharides and three polysaccharides and describe the similarities and differences between these three groups.

13 a Draw the general formula for an amino acid and explain how the R group influences the structure of a protein formed by particular amino acids.

b Explain how a zwitterion forms and how the ionic nature relates to melting point and solubility.

Understanding

14 The arrangement of long-chain molecules in high-density and low-density polyethylene can be represented as shown.



a Explain what causes the difference in density between the two types of polyethylene.

b Which form would you expect to have the greatest mechanical strength? Give your reasons.

c Which type would be more suitable for a:

i washing-up bowl?

ii cordial bottle?

d Explain why a polyethylene shopping bag is a greater hazard to the environment than a paper one.

15 Teflon is the name given to the polymer used to coat kitchenware so it is non-stick. It is formed by reacting tetrafluoroethene in the presence of a catalyst. In this process:

A a condensation reaction takes place producing the polymer and water.

B a condensation reaction takes place producing the polymer only.

C an addition reaction takes place producing the polymer and water.

D an addition reaction takes place producing the polymer only.

16 Which of the following molecules is most likely to undergo condensation polymerisation with itself?

A $(CH_3)_3COH$

B $H_2N(CH_2)_6NH_2$

C $ClOC(CH_2)_4COCl$

D $H_2N(CH_2)_5COOH$

Applying

17 What types of intermolecular forces would you expect in:

a polypropylene?

b poly(vinyl chloride)?

c nylon?

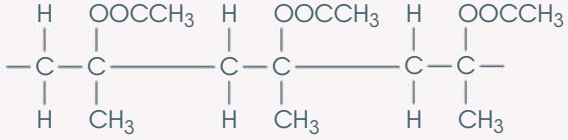
d PET?

18 For each of the structures shown:

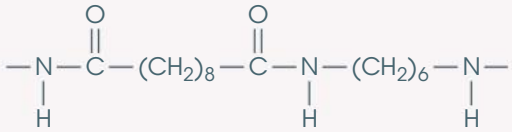
i draw the structure of the monomer(s) from which it is produced.

ii identify the type of polymerisation.

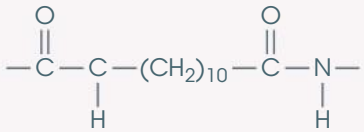
a



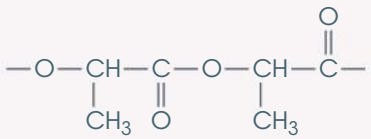
b



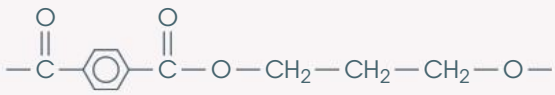
c



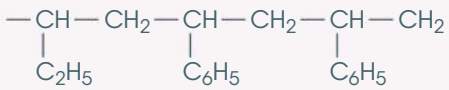
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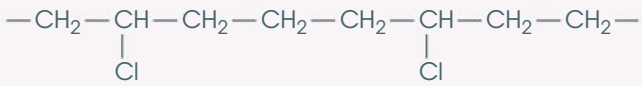
e



f



g



19 Draw the structures of the polymers formed from the following monomers.

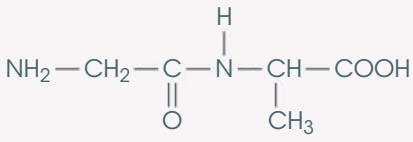
a $CHF{=}CH_2$

b $H_2N{-}(CH_2)_3{-}NH_2$ and $HOOC{-}(CH_2)_4{-}COOH$

c $HO{-}CH_2CH_2{-}OH$ and $HOOC{-}CH_2{-}COOH$

d $CH_3CH(CH_3)C{=}CH$

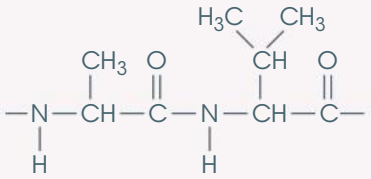
20 Two amino acids glycine (Gly) and alanine (Ala) join to form the dipeptide glycylalanine (Gly–Ala) as shown.



a Copy the diagram and circle and name the bond that joins the two amino acids together.

b Write the equation for the reaction by which this dipeptide hydrolyses back to the original amino acids.

21 Consider the following section of a protein chain.



a Draw and name the amino acids that reacted to produce this section of the protein.

b Draw the zwitterion for each of these two amino acids.

Analysing

22 Predict the type of bonding, if any, that would occur between the polymer chains in Question **18 a** and **b**.

23 Compare the structures of cellulose and starch and explain the difference in their properties in terms of their structure and bonding.

Reflecting

24 Explain why proteins form a tertiary structure yet polyethylene does not.

CHAPTER 8
ANALYTICAL TECHNIQUES



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By the end of this chapter you will have covered the following material.

Science Understanding

- Data from analytical techniques, including mass spectrometry, X-ray crystallography and infrared spectroscopy, can be used to determine the structure of organic molecules, often using evidence from more than one technique (ACSCH130)

8.1 Analytical techniques: faster and better

Chemists have to determine the structures of organic compounds to be able to understand how bonds are formed and how molecules react. This enables a better understanding of how biological molecules such as DNA, enzymes and ribosomes function. Understanding the detail down to the individual atoms has revolutionised the development of new medicines and promises advances in the early diagnosis of cancers.

Key to the success in these medical fields is the instruments that enable chemists to determine the structures. Each instrument provides unique information. When the information from different instruments is combined, a three-dimensional (3D) view of the substance is built up. The chemist's role is to translate the various signals into a structure that makes sense.

The oldest technique is X-ray crystallography; it uses X-rays to determine the structure of isolated crystals. The other techniques are collectively described as organic spectrometry. Each spectrometer monitors the response of the molecule to different energy inputs. In mass spectroscopy, it is high-energy electrons, nuclear magnetic resonance (NMR) spectroscopy uses radio waves, infrared (IR) spectroscopy uses heat energy and ultraviolet (UV)–visible (UV–vis) spectroscopy uses visible or UV light.

Table C8.1 Energy source and data output of the analytical techniques

Technique	Energy source	Data output
X-ray crystallography	X-rays	Diffraction pattern that indicates the 3D structure, bond lengths and bond angles
Mass spectroscopy	High-energy electrons	Peaks correlating to the *m*/*z* ratio that indicate the molar mass and isotopic abundances
NMR spectroscopy	Radio waves	Peaks that are useful for determining the C—H backbone of a molecule
IR spectroscopy	Infrared waves	Bands used to determine the type of bonds and functional groups present. May identify the compounds using spectra as 'fingerprints'
UV–vis spectroscopy	UV–visible waves	Absorption spectra that show the concentration of organic compounds. May identify the compounds using spectra as 'fingerprints'

Mass spectroscopy, X-ray crystallography and NMR spectroscopy have allowed revolutionary breakthroughs in determining structure and function of molecules. Nobel Prizes in Chemistry were often given to the scientists who developed these three techniques. By 2014, X-ray crystallography had been associated with 28 Nobel Prizes.

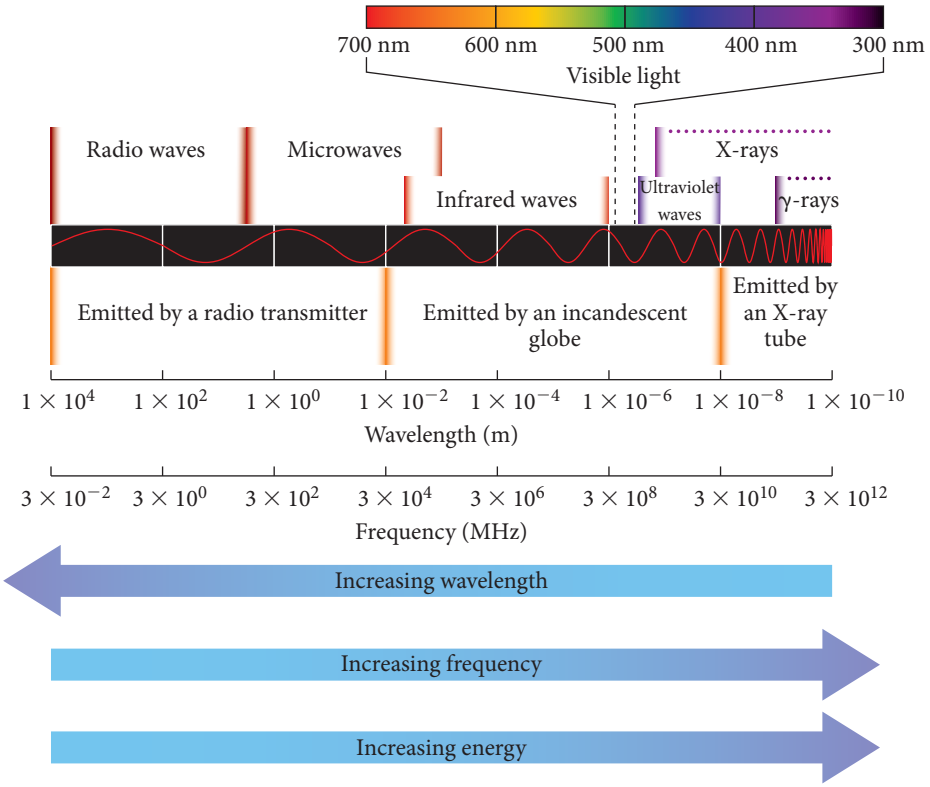
The electromagnetic spectrum

The electromagnetic spectrum is the general name given to the complete range of electromagnetic radiation that is emitted from the Sun. The radiation emitted as waves has a range of energies and wavelengths. We see only a small part of this range called the visible spectrum. The visible part of the spectrum can be split to show the colours of the rainbow. Red light has less energy and a longer wavelength than violet light.

Energy is inversely proportional to the wavelength (the distance between the crests [or the troughs] of the waves). Electromagnetic waves effectively travel at the speed of light. This means

that waves with short wavelengths must have a higher frequency (number of waves passing per second). Over the whole spectrum, radio waves have the lowest energy, lowest frequency and longest wavelengths. Gamma rays have the highest energy and shortest wavelengths.

Spectroscopy techniques rely on the full electromagnetic spectrum. Each instrument uses a particular range of the spectrum that corresponds to the energy used by the technique.



◀ **Figure C8.1**
The electromagnetic spectrum

Note: the wavelength of the waves that make up visible light is so small that it is recorded in nanometres, nm (1 nm = 10^{-9} m). The frequency of the waves has been measured in megahertz, MHz (1 MHz = 10^{6} Hz).

REVIEW TECHNIQUES

Test your knowledge as you learn about the techniques, view videos and animations.

8.2 Mass spectrometry

Mass spectrometry can tell chemists a lot about the structure of a substance, such as the molar mass (M) and elements present, and it can detect the **isotopes** of an element. Mass spectrometry has many uses from radioactively dating fossils to detecting drugs in sport supplements. Mass spectrometers are found in many locations, including on satellites, where they can identify particles intercepted in the solar wind. Mass spectrometry only requires a small amount of material but offers a wealth of information.

Principles of mass spectrometry

The mass spectrometer consists of an ionisation chamber, a path along which the particles travel and a detector.

The vaporised sample is injected into the ionisation chamber where it is bombarded with high-energy electrons that can knock an electron off the molecule or atom. The resultant particle is positively charged and is called a **molecular ion**. Usually only one electron is knocked off, so the charge is typically 1+. If more than one electron is knocked off, then the charge corresponds to the number of electrons removed. In the original molecule, every electron was paired, so when an electron is knocked off, the resulting molecular ion has an unpaired electron. This molecule is called a **radical** and is represented by '·'. See Figure C8.3.

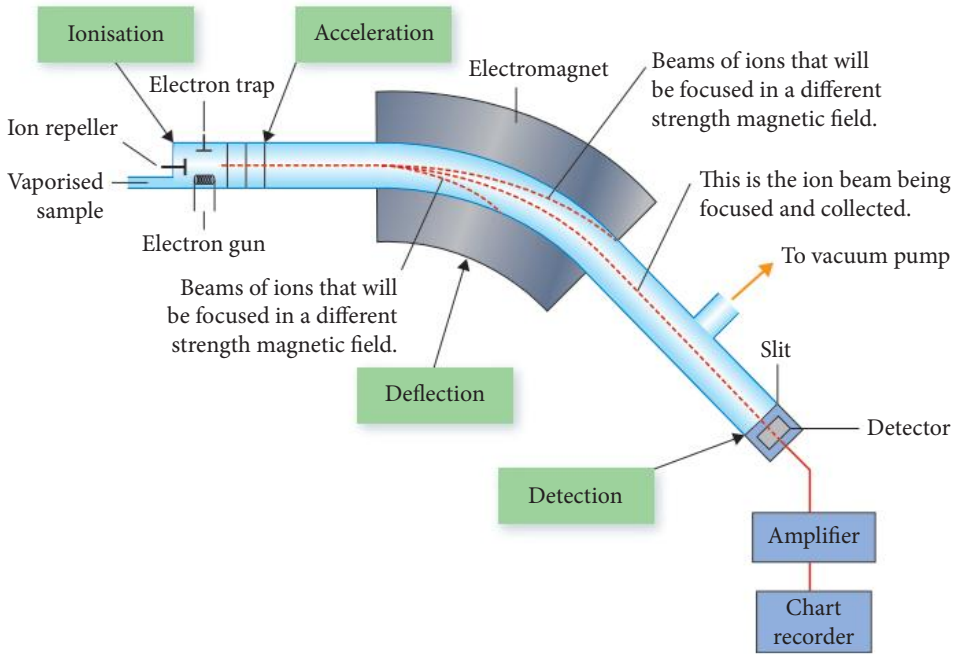


Figure C8.2 ▶
The mass spectrometer – a schematic diagram

$$CH_4 + e^- \rightarrow CH_4^{+\bullet} + 2e^-$$

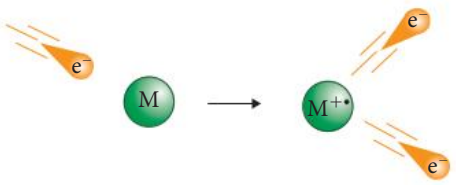


Figure C8.3 ▶
Formation of a positive ion by electron bombardment: M represents an atom or a molecule.

These positive particles are accelerated along the path by an electrical field. They then pass through a magnetic field, which deflects the ions based upon mass (m) and charge (m/z). Smaller, higher charged particles are easier to deflect. By varying the strength of the magnetic field, the ions can be separated by their mass and collected by a detector. The intensity of the ion beam hitting the detector provides a measure of abundance. The results are presented as a mass spectrum: a plot of m/z versus abundance. Only cations are detected.

Mass spectrometry is a technique that produces cations, which are separated according to their mass/charge ratio, and measures their relative intensity.

WOW

Ivory's sense of identity

Elephants face extinction due to the poaching of ivory. Isotope signatures can determine the population of African elephants and region that an ivory specimen came from. The tusks of elephants have a different $^{13}C/^{12}C$, $^{87}Sr/^{86}Sr$ and $^{15}N/^{14}N$ ratios depending on the plants they eat, the rainfall and the soil in the different habitats. This allows identification of legal ivory, which helps to stop the illicit ivory trade. A similar technique is being developed for the Asian elephant and the rhinoceros.

Aboveground testing of nuclear bombs from 1952 to 1962 resulted in an unusually high amount of ^{14}C in the atmosphere. The rate at which this isotope decays is allowing even the age of the tusk to be determined.

The firing of high-energy electrons onto an organic molecule can cause the molecule to fragment. The initial molecular cation can break to form a smaller cation and a free radical. A free radical still has an unpaired valence electron and is very reactive. The free radical is neutral and uncharged so is not detected by mass spectrometry.

The free radical of methane can fragment in a mass spectrometer as shown:

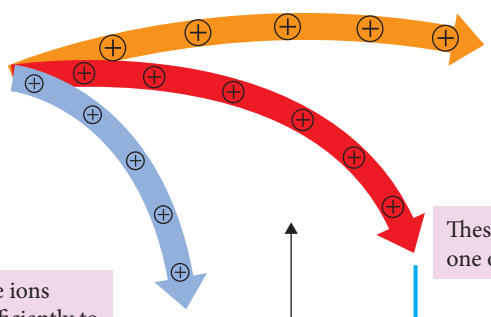
$CH_4^{+\bullet} \rightarrow CH_3^+ + H^\bullet$
or $CH_4^{+\bullet} \rightarrow CH_3^\bullet + H^+$

In these cases, only the CH_3^+ and the H^+ would be detected by mass spectrometry.

WOW

Antioxidants – the buzz

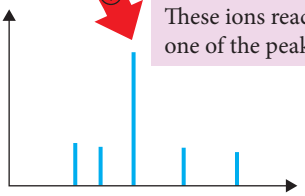
Radicals are produced in your cells by the action of sunlight on skin and eyes as food is turned into energy. Radicals can cause genetic mutations, which may lead to cancer and the signs of ageing. Antioxidants such as vitamins C and E are widely regarded as being able to destroy these radicals. Research has shown that eating whole grains, vegetables and fruit that contain a range of antioxidants provides protection against ageing. Research on the use of supplements over the last 20 years has been inconclusive. Some trials have shown an increase in lung and skin cancers when supplementary antioxidants are taken. Just because antioxidants can react with radicals does not mean they will fix the problem when present in the body. The biochemical pathway and the reactions are far more complex.



In this magnetic field, the mass/charge ratio of these ions is so small that they are deflected too much to reach the detector plate. They are removed by the vacuum pump.

These ions reach the detector plate and produce one of the peaks on the mass spectrum.

In this magnetic field, these ions are too heavy to be deflected sufficiently to reach the detector plate; that is, their mass/charge ratio is too large. They are removed by the vacuum pump.



The other peaks are obtained in a different strength magnetic field.

The greater the proportion of ions in the beam, the higher the peak.

▲ **Figure C8.4** Focusing and collecting an ion stream

ACTIVITY 8.1

USING MASS SPECTROSCOPY

Aim

To show how effective mass spectroscopy can be in developing a new pharmaceutical, fuel, polymer or nanomaterial

What to do

1. In groups of two or three, discuss the problem for about 10 minutes.
2. Research mass spectroscopy and your area of choice, such as the production of a particular pharmaceutical, fuel, polymer or nanomaterial. Find as much information as you need to show the effectiveness of mass spectroscopy.
3. You may find it helpful to browse online spectral libraries via the weblink.

SPECTRAL LIBRARIES

Browse the online library of spectra.

What did you discover?

1. Write a brief account of what you did.
2. Prepare a short presentation aimed at 14–16-year-old students to be delivered to your class. As far as possible, every group member should take part.
3. Be prepared to answer questions and to discuss what you discovered.

Interpreting mass spectra

The plot produced by a mass spectrograph is called a mass spectrum and has a series of lines at different *m*/*z* (mass/charge) values along the *x*-axis. A cation will be detected at the point that corresponds to the mass of the particle, which is the atomic mass unit. The height of the peak corresponds to the abundance of the species. The most abundant peak on the spectrum is called the **base peak** and it is given a relative abundance of 100 per cent. The other peaks are plotted as a relative percentage to the base peak. Mass spectra have a percentage scale on the *y*-axis.

The most important peak on the mass spectrum is the molecular ion ($M^{+\bullet}$) or **parent molecular ion.** This molecular ion gives the molar mass of the original compound.

Fragmentation pattern

Organic molecule fragmentations provide clues to the structure of the molecule. When ethanoic acid ($C_2H_4O_2$) is injected into the mass spectrometer, a range of peaks is observed. Notice that the parent ion at *m*/*z* 60 peak is not the most common peak. The most abundant peak is the base peak at *m*/*z* 43. The other common peaks present are at *m*/*z* 45 and 15.

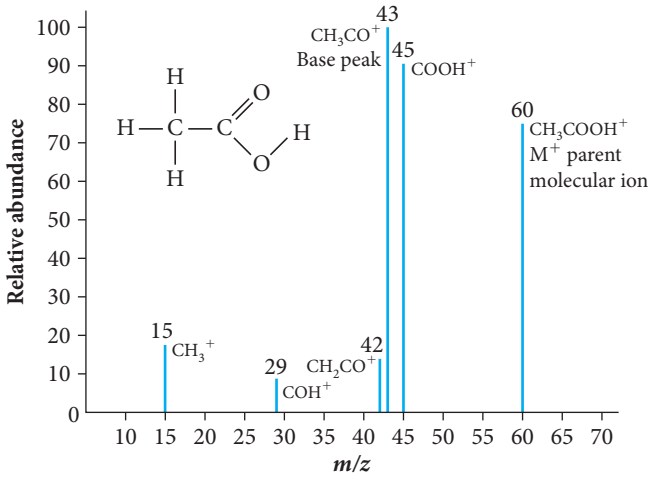


Figure C8.5 ▶ Simplified mass spectrum of ethanoic acid, CH_3COOH. Parent ion and base peak are identified.

The parent ion $C_2H_4O_2^+$ has many different possibilities for fragmentation.

If the bond between the two carbons breaks, then there are two possible peaks, a peak corresponding to the cation CH_3^+ at an *m*/*z* value of 15 and a peak corresponding to $COOH^+$ at an *m*/*z* value of 45. Notice in Figure C8.5 that the peak at 45 is much bigger than the peak at 15. This indicates that the fragmentation:

$$CH_3COOH^+ \rightarrow CH_3^{\bullet} + COOH^+$$

is more common than

$$CH_3COOH^+ \rightarrow CH_3^+ + COOH^{\bullet}$$

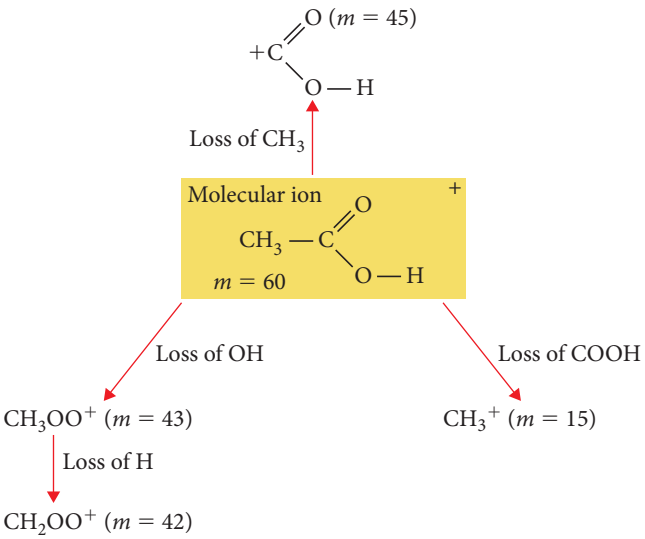
Remember that radicals are not detected by mass spectroscopy.

If the covalent bond between the C and O is broken, then there are two possible fragments:

CH_3CH_2 (*m*/*z* 29) and OH (*m*/*z* 17).

In mass spectroscopy, you can look at the peaks on the mass spectra. A peak of 15 indicates a CH_3^+ and would indicate that the methyl group is present.

To see one way this technique is used, refer to Context 1, 'Wine', page 4.



◀ **Figure C8.6** Simplified fragmentation pattern of molecular ion CH_3COOH^+

Alternatively, you can look at the differences in peak values. The **parent peak** has a value of 60 and there is a peak at 45. This difference, 15, could indicate loss of a methyl group. The peak at 43 is 17 less than the parent peak. This could indicate loss of an OH group. A loss of an H atom could explain a peak at *m*/*z* 59.

Table C8.2 shows common fragmentations that occur in organic molecules.

Table C8.2 Commonly lost fragments for organic molecules

Relative mass	Fragment
15	CH_3
17	OH
29	CH_2CH_3, CHO
31	OCH_3
45	COOH, OCH_2CH_3

INTERPRETING MASS SPECTRA

Watch this video to see how to get information from a mass spectrum.

Elements and their isotopes

In 1920, the mass spectrometer was used to determine masses and relative abundances of isotopes. Francis William Aston was awarded the Nobel Prize in 1922 for his discovery of isotopes in non-radioactive elements, using the mass spectrometer. We now know the main isotopes of each element and their percentages. Aston used ^{18}O as the standard of mass but now ^{12}C is used. The most common isotope of carbon, ^{12}C, has a relative abundance of 99 per cent.

MIXED RECEPTION

Watch the video to see if you can put together all the clues and solve a murder mystery.

Scientists can select particular isotopes. Concentrated samples of isotopes are used as tracers in biology, chemistry and medicine. Radioactive iodine ^{23}I, ^{25}I or ^{31}I is used to test or treat particular thyroid conditions. Mass spectrometry is used to confirm the percentage of each isotope.

Where the ^{12}C ion hits the detector is considered to be at 12 **atomic mass units (amu)**. This isotope is considered to have a relative isotopic mass (RIM) of 12.

From amu to molar mass

The number of lines in a mass spectrum of an element shows the number of different isotopes. The position of the peaks indicates the relative isotopic mass and the height of the peaks indicates the relative abundance of each isotope. This was studied in *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 1.

The relative isotopic mass (I_r) of an isotope is the mass of that atom relative to the mass of an atom of ^{12}C, where ^{12}C has exactly 12 amu.

Every time an element is injected into the mass spectrometer, you would expect the same spectra. This is because the source of the element does not matter; the isotopes are the same and are present in the same proportions. The ratio of the peaks can help identify the element present.

Recall from *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 1 that the weighted average of an isotope's mass or the **relative atomic mass, RAM (A_r)** can be calculated for each element. The RAM takes into account the number of different isotopes and their relative abundances.

A weighted average is similar to the arithmetic mean but takes into account the relative amounts or abundance of each isotope. For example, if a teacher weighed 100 kg and a student weighed 50 kg, then the average would be 75 kg. But if there were 25 students and one teacher, then the average would have to be closer to 50 kg or more precisely:

$$\frac{(50 \times 25) + (1 \times 100)}{26} = 51.9\,\text{kg}$$

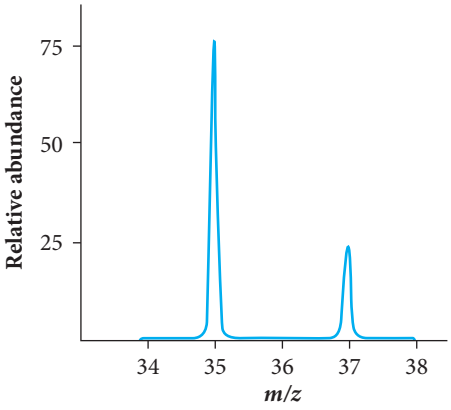
The A_r and amu do not have units. The RAM is usually the value given on the periodic table. This is the value you used for your calculation of molar mass, which has the unit $g\,mol^{-1}$.

Table C8.3 The isotopic composition of common elements

Element	Isotope	Relative isotopic mass	Abundance (%)
Hydrogen	^{1}H ^{2}H ^{3}H	1.0078 2.0141 3.0160	99.99 ~0.01 $\ll$0.02
Carbon	^{12}C ^{13}C ^{14}C	12.000000 13.003 14.003	98.93 1.07 $\sim 10^{-10}$
Oxygen	^{16}O ^{17}O ^{18}O	15.995 16.999 17.999	99.757 0.038 0.205
Chlorine	^{35}Cl ^{37}Cl	34.969 36.966	75.78 24.22
Bromine	^{79}Br ^{81}Br	78.918 80.916	50.69 49.31

WORKED EXAMPLE 8.1

a Use the mass spectrum of chlorine shown in Figure C8.7 to determine its relative atomic mass.



◀ **Figure C8.7** Mass spectrum of chlorine

b Given the RAM of copper is 63.54, work out the percentage abundance for the two isotopes, which have RIM of 63 and 65. (The actual masses are 62.95 and 64.95; four significant figures.)

Answers

a RAM chlorine = 35.45 amu

Logic

1 Determine the number of isotopes and their isotopic masses from the mass spectrum.

Chlorine has two isotopes. ^{35}Cl has a relative abundance of 75.78%. The ^{37}Cl isotope has a relative abundance of 24.22%.

2 Determine the average molar mass (M) for chlorine.

$$\text{Average} = \frac{\text{relative isotope mass}_1 \times \%\text{ abundance} + \text{relative isotope mass}_2 \times \%\text{ abundance}}{100}$$

3 Insert numbers into formula.

$$A_r = \sum \frac{(\text{RIM} \times \%\text{ abundance})}{100}$$

$$= \frac{(35 \times 75.78 + 37 \times 24.22)}{100}$$

$$= 35.45 \text{ amu}$$

b The % abundance for the ^{63}Cu isotope is 73%.

The % abundance for the ^{65}Cu isotope is 27%.

1 Insert numbers into formula.

$$A_r = \sum \frac{(\text{RIM} \times \%\text{ abundance})}{100}$$

$$63.54 = \frac{(63 \times X + 65 \times (100 - X))}{100}$$

2 Add like terms, simplify and make X the subject of the equation.

$$6354 = 63X + 6500 - 65X$$

$$2X = 6500 - 6354$$

$$X = \frac{146}{2} = 73\%$$

The % abundance for the ^{63}Cu isotope is 73%.

The % abundance for the ^{65}Cu isotope is 27%.

Try these yourself

Magnesium has three isotopes with RIM 24, 25 and 26. The relative abundances are 79, 10 and 11%, respectively.

a Calculate the RAM of magnesium.

b Draw the expected mass spectrum of magnesium.

QUESTION SET 8.1

Remembering

1 a Define the following terms.
- **i** amu
- **ii** RAM
- **iii** Molecular ion

b State the meaning of:
- **i** mass/charge ratio.
- **ii** base peak.

2 Draw a simple schematic diagram of a mass spectrometer. Label it to show what happens in each part of the instrument.

3 Which peak in a mass spectrum indicates the molecular mass of the compound?

4 When do you get a peak larger than the parent molecular ion?

Understanding

5 Why are only cations detected in mass spectroscopy?

6 Explain how a mass spectrum can be used to help determine the structure of a compound.

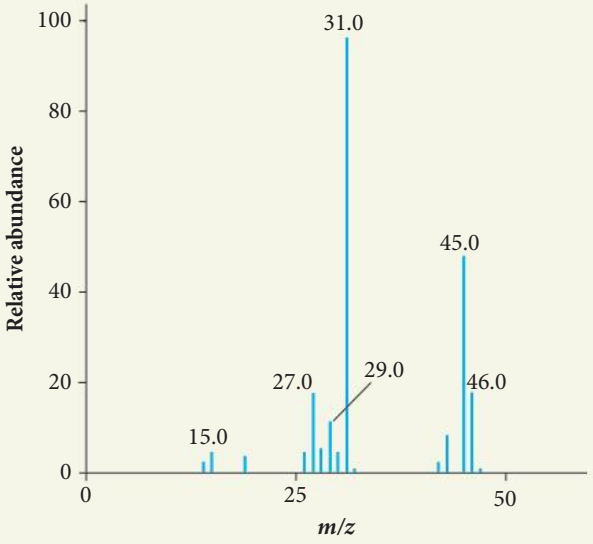
Applying

7 Figure C8.8 shows the mass spectrum of ethanol.

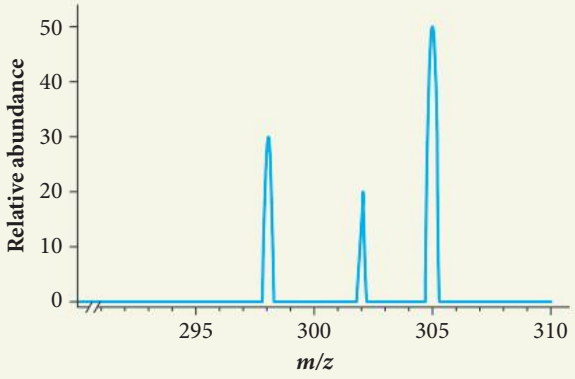
Account for the peaks at 15, 29, 45 and 46.

What can be concluded about the peak at 31? Justify your answer.

8 A scientist was hopeful that she discovered a new element in a meteorite she found on the Nullarbor Plain. Although the largest elements are very unstable, she managed to run a mass spectrum (Figure C8.9) to discover that it had three naturally occurring isotopes. She called it Q after her home state and the queries she had about it. Determine the RAM for Q.

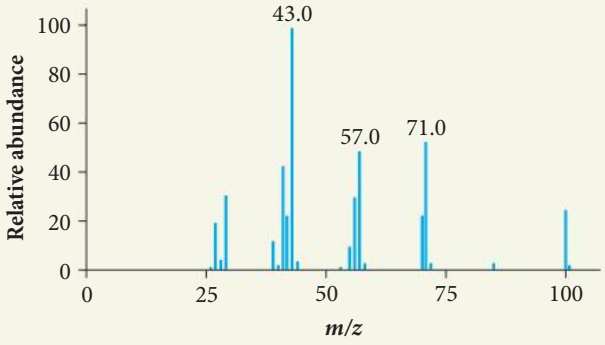


▲ **Figure C8.8** Mass spectrum of ethanol



▲ **Figure C8.9** Mass spectrum of unknown substance Q from a meteor

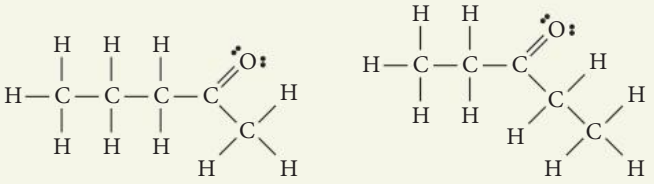
9 Figure C8.10 shows the mass spectrum for C_7H_{16}. Account for the main peaks in the spectrum.



◀ **Figure C8.10** Mass spectrum for C_7H_{16}

Analysing

10 The chemical composition of a compound X was found to be $C_5H_{10}O$. The two possible structural isomers are shown in Figure C8.11.



◀ **Figure C8.11** Possible structures for compound X

- **a** What mass/charge ratio (*m*/*z*) would you expect for the parent ion for each isomer?
- **b** The base peak for structure A occurs at a mass/charge ratio of 43, whereas the mass spectrum for structure B occurs at a mass/charge ratio of 57. Account for these two peaks.
- **c** The mass spectrum of compound X was found to not have a peak at 29. How does this enable the structure of compound X to be determined?

Reflecting

11 How has medicine been advanced due to the technique of mass spectrometry?

8.3 X-ray crystallography

The most famous molecule's helical shape was determined by the analysis of X-ray crystallography of the DNA crystal. Rosalind Franklin's work was used to determine the structure of DNA, RNA, viruses, coal and graphite. Her image from the X-ray crystallography of DNA was the key in determining the structure of DNA. Understanding the structure then helped explain how genetic information is passed from parents to offspring.

In 1962, two Nobel Prizes were awarded to people who used X-ray crystallography to determine structure of biomolecules. The Nobel Prize for medicine went to Francis Crick, James Watson and Maurice Wilkins 'for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material'. The Nobel Prize for chemistry went to Max Perutz and John Kendrew 'for their studies of the structures of globular proteins', namely haemoglobin and myoglobin.

Today, X-ray crystallography is still considered the most accurate method for determining structures. It is used in rational drug design and to work out the structures of proteins, enzymes and viruses. By knowing where the atoms are placed, scientists can determine how these molecules interact so this speeds up the development of new drugs and vaccines, saving millions of dollars.

Atoms are extremely small, with diameters of about 0.2–0.5 nm. Haemoglobin has a relative molecular mass of 67 000 and dimensions of 6.4 × 5.5 × 5.0 nm. Ribosomes are much larger, but more complex. The challenge is to distinguish individual atoms in order to resolve how molecules are put together.

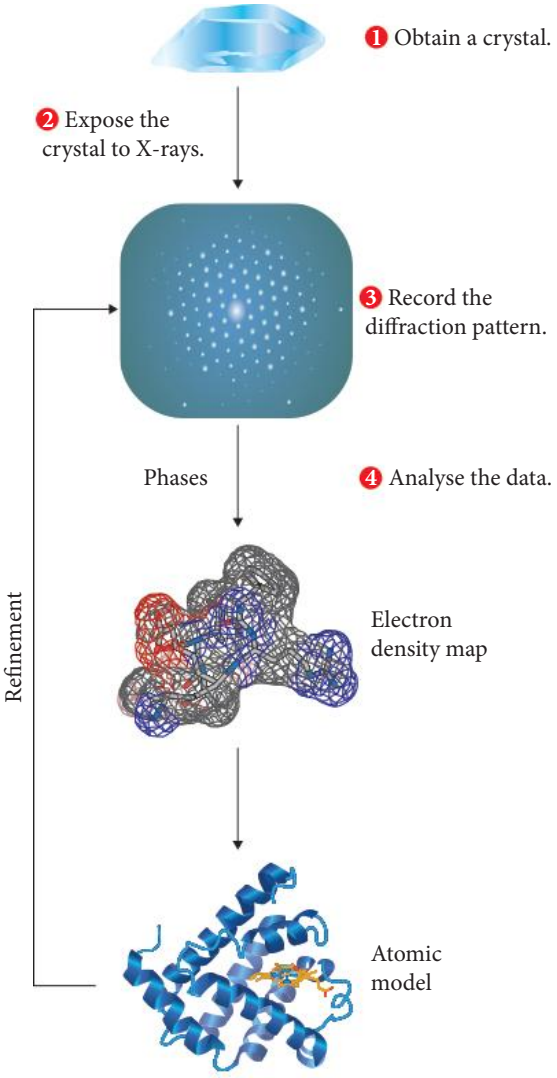


Figure C8.12 ▲ An X-ray diffraction flowchart

Figure C8.13 ▶ The 1915 Nobel Prize in Physics was awarded to Sir Henry Bragg and Lawrence Bragg for the development of the X-ray spectrometer, which showed that salts such as potassium chloride crystals have a regular array.

Principles of X-ray diffractometry

There are four major steps in an X-ray study.

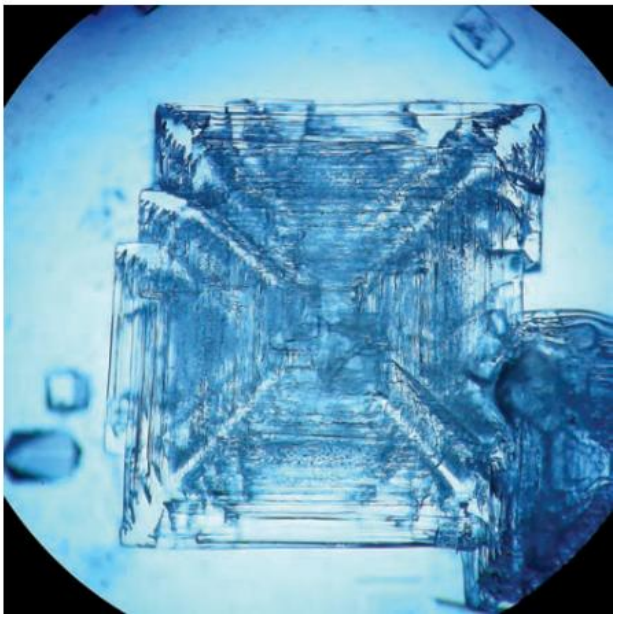
- Obtain a crystal of the matter being studied.
- Expose it to X-rays.
- Record the diffraction pattern. Diffraction is the pattern observed when X-rays act as a wave and are scattered by layers of atoms within the crystals.
- Analyse the data. Computers are used to analyse the data and propose a structure. The computers iterate (complete the measurement and recording numerous times) to produce the best structure. The whole process takes a lot of time and money.

Producing crystals

For X-ray diffraction to work, a crystal has to be produced. A crystal is a regular array in which the molecules or atoms line up in a repeating pattern. Dr Franklin used the sodium salt of DNA to produce a crystal for her work on DNA structure. Producing a crystal is a very difficult task. The crystal must be near perfect and small (0.1–0.5 mm).

Producing a crystal is a time-consuming task; 'small' molecules, such as cholesterol and fatty acids, are easier to produce than larger ones, such as DNA, proteins and viruses. When crystallising a biomolecule, the pH, ionic strength, nature of the precipitant, temperature and presence of cofactors or counter ions must be taken into account when attempting to grow a good-quality crystal. The crystal may even need to be stabilised by freezing in liquid nitrogen.

Typically, crystals are formed by cooling supersaturated solutions of the substance. Care must be taken to ensure that the individual crystals are big enough to be used. The Australian Synchrotron in Clayton, Victoria, is sensitive enough to use very fine crystals.



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Diffraction

A crystal of potassium chloride (KCl) (Figure C8.13) is placed in the path of a beam of visible light; the light passes right through it virtually unchanged. The wavelengths in white light are much longer than the interparticle distances in KCl. But if the same crystal is exposed to X-rays, two things occur.

The energy of the X-ray is similar to the energy of the electrons in their orbitals. So a small fraction of the radiation is absorbed and re-emitted by the electron clouds of the atoms present. This effect leads to fluorescence.

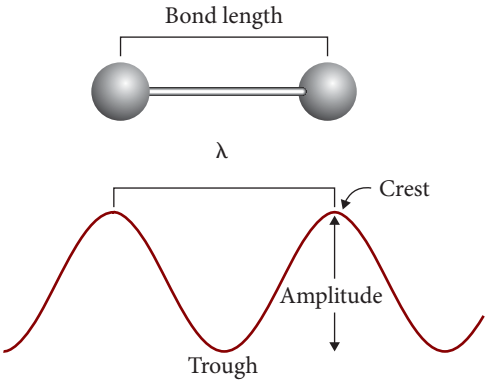
The interference of scattered X-rays also leads to **diffraction**. Diffraction is the apparent scattering of waves when they encounter objects in their path. This is seen when sunlight hits a thin layer of oil on water or in soap bubbles (Figure C8.15). The incident light will be reflected from the top and the bottom of the oil layer. The beams from the bottom must have travelled a further distance. If the two waves come together, then the crests of the waves may reinforce each other. This is called constructive interference. If one crest is out of phase with the other, then they will cancel each other out. This is called destructive interference.

X-RAY CRYSTALLOGRAPHY

Watch this video, which introduces X-ray crystallography.

UNSUNG TECHNIQUE

Read about the story of crystallography.



▲ **Figure C8.14** The wavelength of the X-rays is approximately equal to the bond length between atoms.

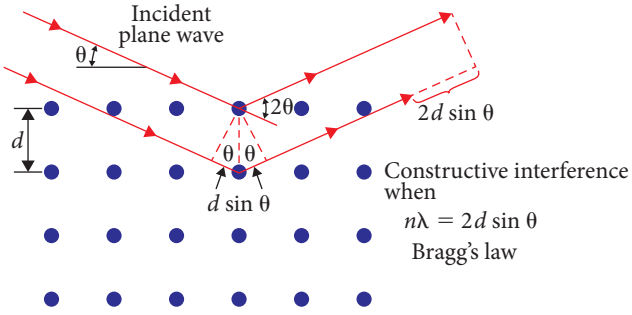


angelo lano/Shutterstock.com

▲ **Figure C8.15** Diffraction in a soap bubble

- For each crystal, there will be only certain angles of incidence that allow constructive interference. At these angles, a relatively strong reflection is observed. At the other angles, no scattered beam will be seen.

Diffraction occurs when the object has a similar dimension to the wavelength being used. X-rays are used because their wavelength is very similar to the distance between atoms (Figure C8.14). The electrons are primarily responsible for the scattering of X-rays. The electron density (number of electrons in a given volume) determines how strongly an atom scatters X-rays.



◀ **Figure C8.16** Reflection in a crystal

The angle of reflection is equal to the angle of incidence.

WOW

The parent trap

The youngest ever Science Nobel laureate is Lawrence Bragg, born in South Australia. In 1915, at the age of 25, he and his father William Bragg received the Nobel Prize in Physics for their work in X-ray crystallography. It took him years to get true recognition as many thought nepotism had played a role. Pierre and Marie Curie had recently discovered radium and radiation. William Bragg and others thought X-rays were particles. Diffraction patterns were observed but no one could work out what they were due to. Lawrence explained the diffraction patterns in the 3D layers of the crystal, formulating his Bragg equation and confirming that X-rays are waves.

Lawrence succeeded Rutherford as the Cavendish Professor in Cambridge, where he championed molecular biology by means of X-ray crystallography. His four researchers John Kendrew, Max Perutz, Francis Crick and James Watson achieved their own Nobel Prizes in 1962.

THE BRAGG EQUATION

Watch the video commemorating a century since the publication of the Bragg equation.

Source of X-rays

X-rays can be produced in the laboratory from X-ray tubes or synchrotrons.

When extremely high-energy electrons are fired at particular metals, electrons can be knocked out from the metal's electron shells. Electrons in higher shells with greater energy can transition to the lower shell by emitting energy. You will recall atomic absorption spectroscopy (AAS) and emission spectra from *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 1. The energy of the electromagnetic radiation released is due to the difference in the energy of the shells. In emission spectra and AAS, the energy is in the visible part of the spectrum. X-rays have much greater energy than visible light. They are produced when the high-energy electrons eject electrons from the lower atomic energy levels of heavy metals.

Another type of X-ray radiation is produced when these high-energy electrons hit the metal. As the bombarding electrons fired at the metal de-accelerate, they may also release excess energy as X-rays.

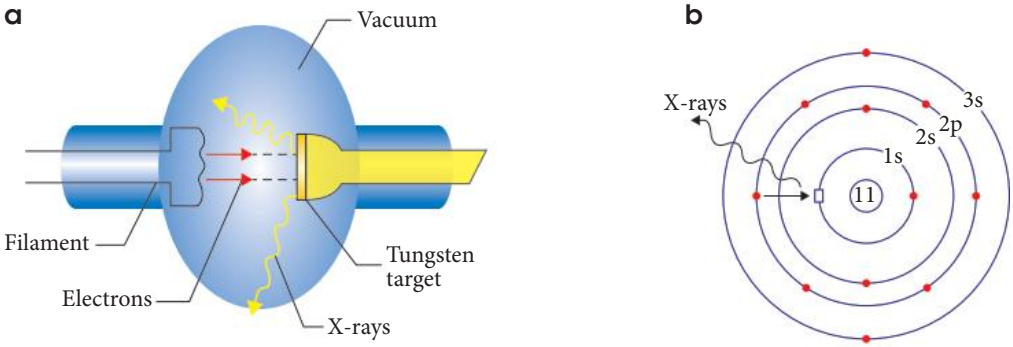
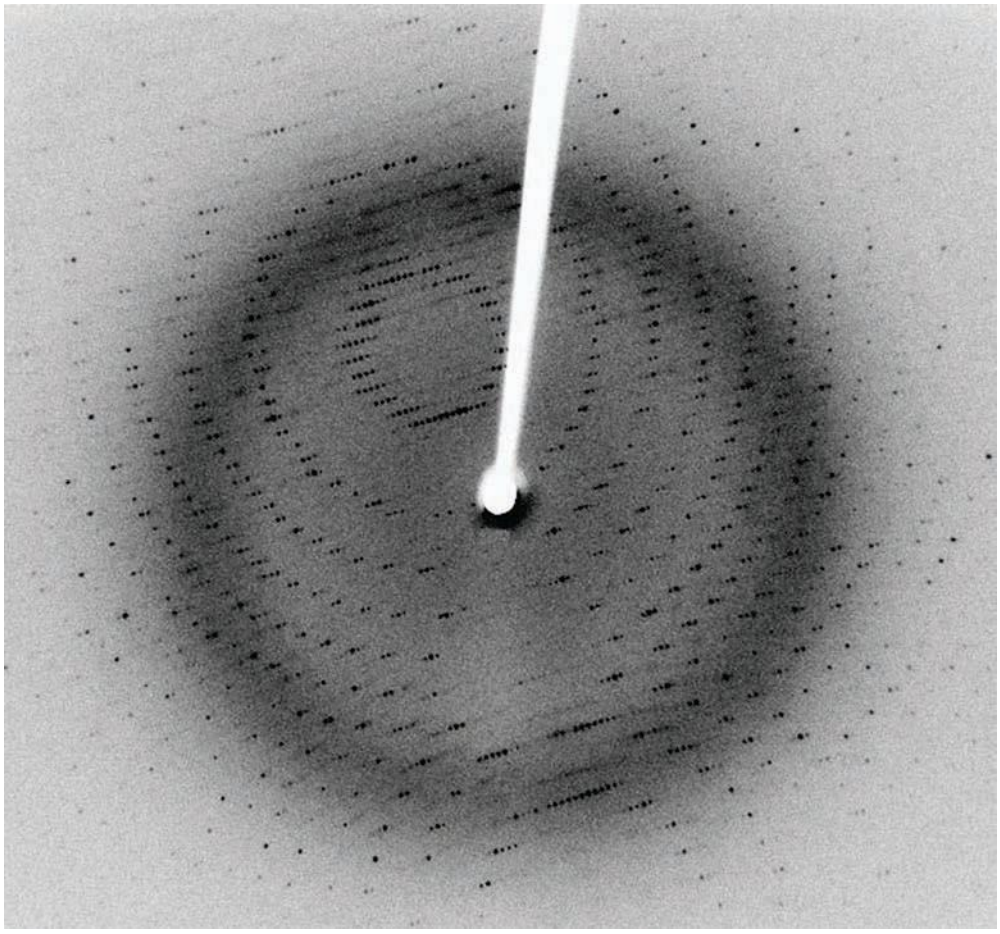


Figure C8.17 ▼
a) An X-ray tube; b) X-ray produced when the incident electron has sufficient energy to remove a 1s electron. The place will be refilled by an outer-shell electron and produce X-ray radiation; c) Diagram of a synchrotron; d) An electron energy of 3 GeV was chosen for the Australian Synchrotron storage ring to allow for the production of light at frequencies that encompass a wide range of the electromagnetic spectrum, from far infrared to hard X-rays.

Synchrotrons are machines that accelerate charged particles such as electrons to extremely high energies and speeds that approach that of light. The electrons are accelerated by strong magnetic and electrical fields. They accelerate around circular orbits. And as they change direction, they are forced to release energy as part of the electromagnetic spectra. The synchrotron is a more powerful source, not only because the light is 1000–10 000 times brighter than in a laboratory, but also because scientists can choose the wavelength so that the best match is made for the sample being studied.



Jeff Dahl/Wikimedia Commons/CC-BY-SA-3.0

◀ **Figure C8.18**
An X-ray diffraction pattern

To see why crystallography was important in determining chemical structures, refer to Context 4, 'Polymer chemistry', page 86.

Interpreting diffraction patterns

Early experimenters such as Lawrence Bragg had to calculate the dimensions between the ions without computers, manually turning the crystals and calculating the intensity between each layer to build up a three-dimensional view. With a lot of time and calculation, they could show that diamonds have tetrahedral carbons and salt crystals consist of atomic lattices and not, as had been imagined, molecular ones.

Today, the crystal in the X-ray machine is automatically rotated, producing diffraction patterns. Detectors measure hundreds of reflections at once, reducing the time needed from weeks to days. With intense light sources such as the synchrotron, the time needed to collect data is also reduced further to seconds.

From the diffraction pattern, an electron density map can be made. This allows the distance between the atoms to be calculated so bond length and bond angles can be determined.

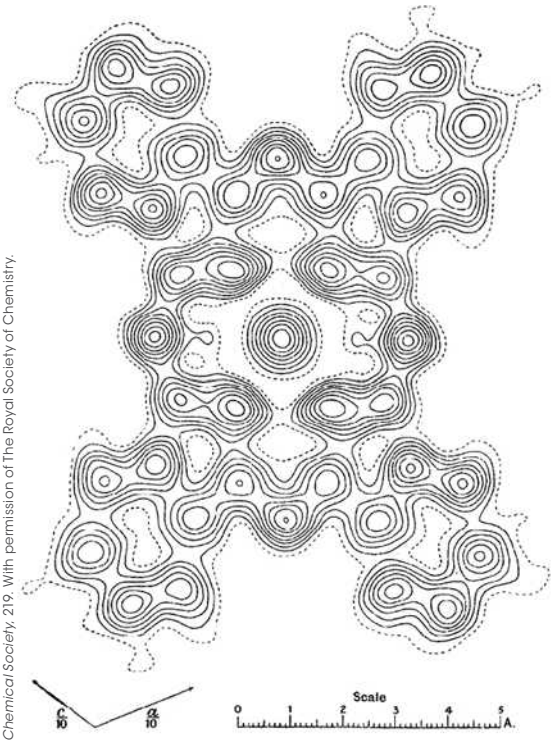
X-ray crystallography calculates the structure of molecules. Interpretation of diffraction patterns observed when X-rays are scattered by the electrons in a crystal allows bond angles and lengths to be determined.

AUSTRALIAN SYNCHROTRON

Find out about the Australian Synchrotron and projects underway.

Figure C8.19 ▶
a) The resultant electron density map and b) determined structure (M = metal atom). Atoms with higher atomic numbers have more electrons so scatter X-rays more effectively. Electron density maps provide the location of atoms relative to each other, allowing the bond angles and lengths to be determined. Note that hydrogen atoms are not often located due to their small size.

a



Reproduced from Robertson, J. M. & Woodward, I. (1937) An X-ray study of the phthalocyanines. Part III. Quantitative structure determination of nickel phthalocyanine. *Journal of the Chemical Society*, 219. With permission of The Royal Society of Chemistry.

b

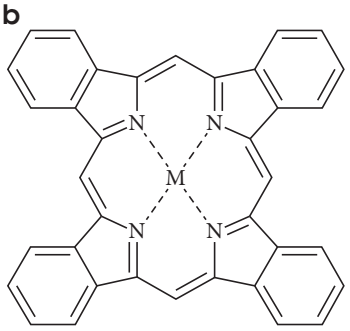
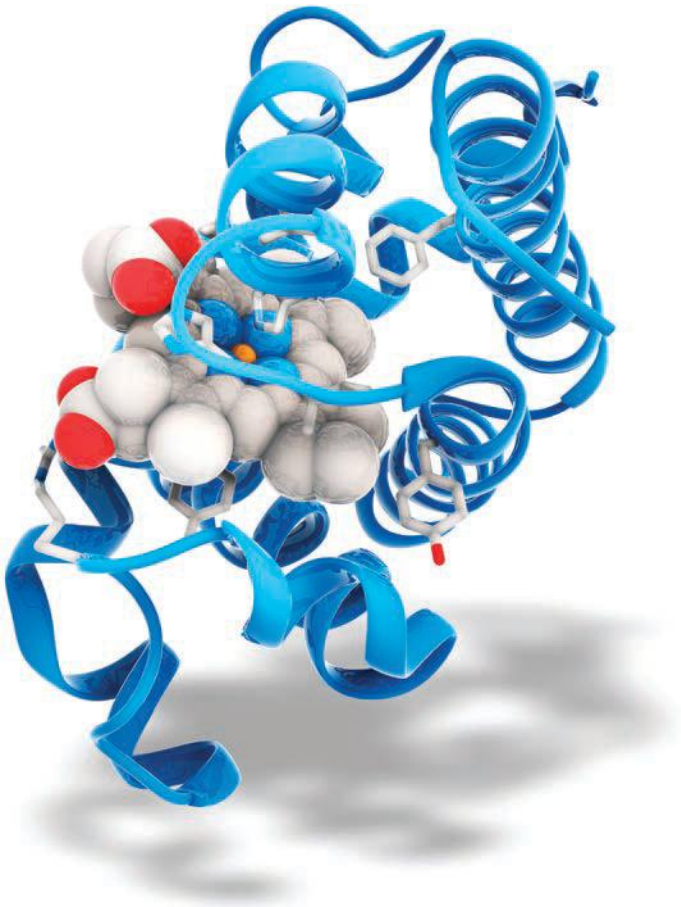


Figure C8.20 ▶
The final 3D structure of the biomolecule myoglobin determined by X-ray crystallography



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INTERNATIONAL YEAR OF CRYSTALLOGRAPHY

Visit the website for the latest news on the International Year of Crystallography.

QUESTION SET 8.2

Remembering

1 How can X-rays be produced?

2 What part of the electromagnetic spectrum is used to determine the bond lengths between atoms in proteins?

3 What factors affect the quality of crystals?

Understanding

4 Describe a process that could be used to make a crystal of NaCl.

5 What is one advantage and one disadvantage of X-ray crystallography compared to other techniques?

6 Why is a crystal of a ribosome more difficult to prepare than an ionic salt?

Applying

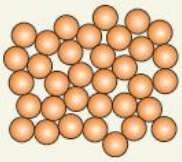
7 Would the crystals prepared for X-ray crystallography have the same shape if produced under different conditions?

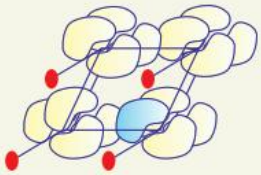
8 What areas of research is the X-ray crystallography technique used for?

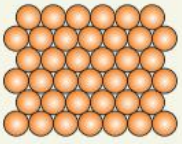
Analysing

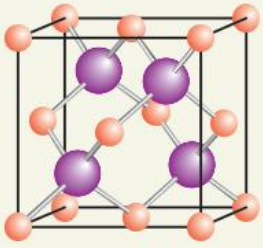
9 Crystals have to have a regular array. Which of the following shapes would not make a good crystal?

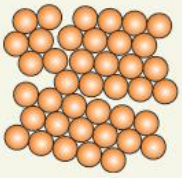
a 

b 

c 

d 

e 

f 

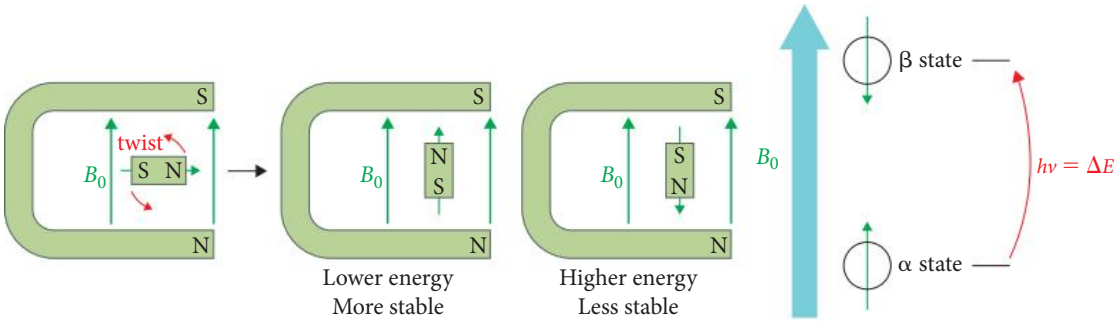
8.4 NMR spectroscopy

One of the most important and powerful techniques used to determine the structures of molecules is nuclear magnetic resonance (NMR). In 1991, the Nobel Prize in Chemistry was awarded to Richard Ernst. He developed the most powerful tool for the determination of the structure of organic and inorganic compounds and biological macromolecules in solution. His work enabled this technique to become an alternative to X-ray crystallography. It relies on the behaviour of nuclei when placed into a magnetic field. It has been likened to the nuclei playing their own faint, magnetic melody. The atoms are identified by a characteristic melody that they emit. Ernst's trick was to make this music audible; he allowed chemists to pinpoint the exact location of nuclei within hundreds of others in complex molecules.

Principles of NMR spectroscopy

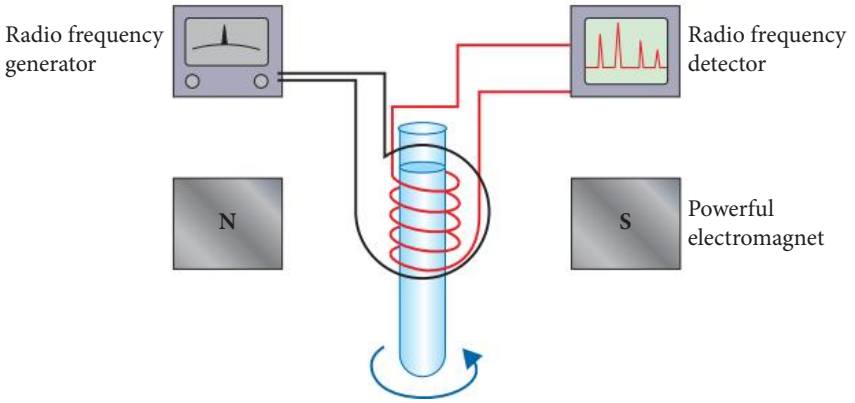
When matter is placed in a magnetic field, some nuclei act like microscopic magnetic compass needles. The charged nuclei spin and create small magnetic fields. Only nuclei with an odd number of **nucleons** (protons and neutrons) possess spin that creates the magnetic field. The most common nuclei studied are ^{1}H and ^{13}C. Just like iron filings near a magnet, most nuclei align with the field. This is the lower energy state. Nuclei aligned with the field can absorb the energy of the radio wave and flip to a higher energy spin (not aligned) when the radio waves have the exact frequency that matches the resonance of the nuclei. The energy difference between these two spins depends upon the nature of the nuclei and chemical environment of the nuclei.

Figure C8.21 ▼ Hydrogen nuclei in an external field act like small magnets. Nuclei aligned with the field have less energy and are more stable. The nuclei aligned against the field have higher energy and are less stable.



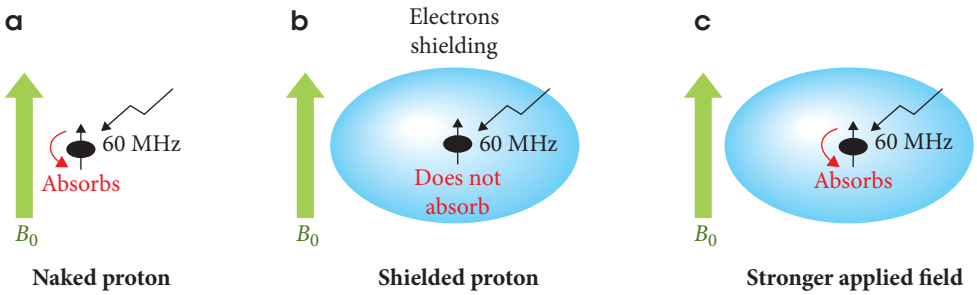
The NMR spectrometer consists of a large magnet, a sample holder, a source of radio waves and a detector. The sample is placed into the magnetic field. The sample will be irradiated with a range of different frequencies of radio waves. A number of different frequencies will be absorbed as particular nuclei flip. The detector records the waves emitted when the nuclear spin returns to the lower energy state. This produces NMR spectra that show series of lines correlating to the type and the environment of the nuclei.

Figure C8.22 ▶ A simplified NMR spectrometer



Chemical environment

The energy required to flip the nucleus indicates the chemical environment of the nucleus. When protons are in an identical environment, they will absorb the same frequency and produce one peak.



◀ **Figure C8.23**
a) A naked proton will absorb the energy from the radio waves and flip to the higher energy state. b) The presence of electrons will shield the proton. The same amount of energy will not be sufficient to flip the proton to the higher energy state. c) A stronger field is now required to compensate for the shielding and to cause the proton to flip.

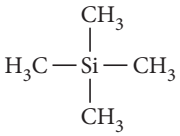
Electrons are also spinning charged particles and produce a small magnetic field. The electron clouds close to the nuclei can **shield** the proton from the effect of the field. Shielded nuclei would require higher energy to be flipped.

If all protons were in the same chemical environment, we would not get much information. Each atom involved in a chemical bond shares electrons. Protons are not in the same environment unless they are bonded to the same group of atoms in the same way. Polarity is an important factor in the chemical environment of the nuclei as it affects the sharing of the electrons.

Chemical shift

The most shielded compound is $Si(CH_3)_4$, called **tetramethylsilane (TMS)**. Silane is less electronegative than carbon so the bonding electrons will spend more time around the hydrogen nuclei. In this compound, the 12 H atoms in the same chemical environment give a strong signal. TMS is used as the zero and is the calibration peak generally shown in every spectrum.

All protons in organic molecules absorb downfield (to the left) of the TMS signal. All other protons would be less shielded than those in TMS and this difference is called the **chemical shift, symbol δ (delta)**. Chemical shift is the ratio of the shift downfield from TMS (Hz) to total spectrometer frequency (Hz). Chemical shift is measured in parts per million (ppm). It is called the delta scale.



▲ **Figure C8.24**
Tetramethylsilane is the standard used in NMR spectroscopy. As Si is less electronegative than C, it has the least shielded signal and is used as the 'zero' in NMR spectra. All other organic signals are shifted to the left of TMS.

The technique of nuclear magnetic resonance spectroscopy is due to nuclei in a magnetic field being forced to 'flip'. Electrons shield the nuclei, which alters the resonance/chemical shift, allowing determination of structure.

The chemical shift has the same value regardless of the strength of the field. So a type of proton in a 60, 100 or 300 MHz NMR spectrometer will have the same chemical shift.

Solution

The main advantage of NMR spectroscopy over X-ray crystallography is that it does not require crystals of the molecules. Molecular structure can be determined in solution. ^1H are very common, so we need to isolate the signal of the compound being studied from the signal of the solvent being used. Chemists use a solvent that has no magnetic dipole moment, which would be due to protons and neutrons cancelling out. The use of an alternative isotope of hydrogen, ^2H or deuterium (D), to make solvents such as D_2O (10 protons, 10 neutrons) and CD_2Cl_2 (42 protons, 42 neutrons) produces a solvent invisible to the NMR spectrometer.

Interpreting NMR spectra

NMR spectroscopy is used to determine the structure of an organic compound and is able to distinguish between isomers. When a compound is irradiated with radio waves of different frequencies, a number of different frequencies will be absorbed. When these are emitted, they will produce a number of peaks on the spectrum. The spectrum produced shows the calibration peak and a series of lines along the horizontal scale labelled chemical shift.

Tables like Table C8.4 are used when interpreting NMR spectra.

Table C8.4 Typical protons shifts values relative to TMS = 0. The solvent used may produce slightly different values so these are a guide only. Where more than one proton environment is shown in the formula the shift refers to the ones in bold letters. Ar = aromatic group.

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
Alkane C**H**$_3$	0.9	R—N**H**$_2$ RCH=C**H**$_2$ 4.6–6.0	Variable, about 1.5–4
Alkene C**H**$_2$—R	1.3	R—O—C**H**$_3$ or ROCH$_2$R	3.3
R—C=OC**H**$_3$	2.1	R—O**H**	Variable, about 1–6
R—C**H**$_2$—X (X = F, Cl, Br or I)	3–4	Ar—O**H**	Variable, about 4–7
C**H**$_3$—COOR	2.0	R—COO**H**	9–13
RC**H**$_2$OH RCH=CH—C**H**$_3$	3.3–4.5 1.6–1.9	R—C(O)**H**	9–10

Low-resolution ^{1}H NMR spectroscopy

Low-resolution ^{1}H NMR spectroscopy is the most common instrumental technique used. The ^{1}H or proton is very abundant and hydrogen is usually very common in organic molecules. Low-resolution NMR spectroscopy can determine the chemical environment of the nuclei (such as an —OH or a —CH$_2$—), the number of these environments and the number of protons in each environment.

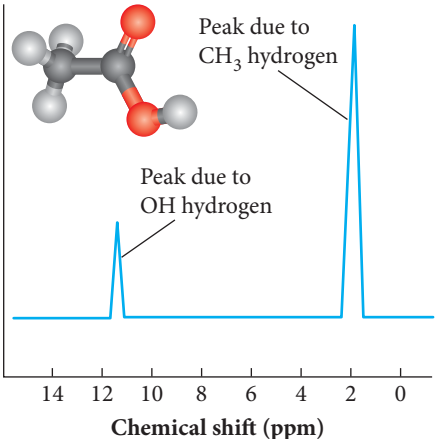
In NMR spectroscopy, the ^{1}H or proton refers to the hydrogen nuclei. The bonding electrons are still orbiting the nucleus. They provide the shielding. It is not referring to the H^+ ion. It is in acid–base reactions that the proton transferred is the H^+ ion.

The number of peaks

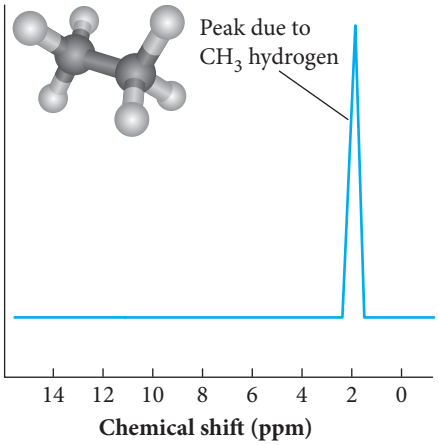
The number of peaks shows how many different kinds of chemical environments are present. If the protons are in the same environment, they will produce a peak with the same shift so are seen as one peak.

From Figure C8.25, you can see that there are four H atoms in ethanoic acid (CH$_3$COOH). Three are attached to the same carbon, forming a methyl group and one is attached to the oxygen, forming the hydroxyl group. There are two hydrogen environments so there are two peaks in the spectrum.

For ethane, shown in Figure C8.26, there two methyl groups, which is a total of six hydrogens. Due to the symmetry of the molecule, one hydrogen chemical environment is present.



▲ **Figure C8.25** The low-resolution ^{1}H NMR spectrum of ethanoic acid (simplified)



▲ **Figure C8.26** The low-resolution ^{1}H NMR spectrum of ethane (CH$_3$CH$_3$)

The location of peaks

The *location* of the signal shows how shielded or deshielded the proton is. The list of typical proton shifts, as shown in Table C8.4, can be very valuable for determining the types of protons present.

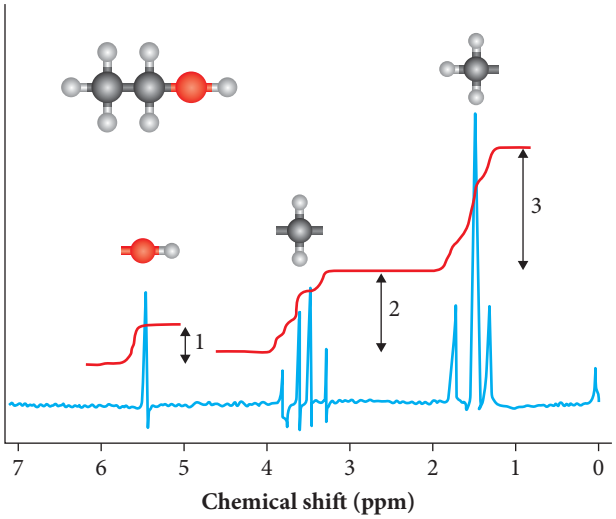
For ethane (Figure C8.26), the spectrum shows a peak less than 1 ppm. This is caused by the hydrogen protons (^{1}H) in the methyl group. The protons are all attached to a carbon and are still relatively shielded but are still downfield from TMS.

In ethanoic acid, a peak is present, at about 2 ppm, for the protons in the methyl group. Next to this methyl group is a carbon with two oxygens attached. When oxygen is attached to the carbon, it attracts the electrons and the nuclei are less shielded. It takes less energy to flip the nuclei. So the methyl protons are slightly further downfield than those in ethane.

In an ethanoic acid spectrum, there is a peak near 12 ppm. This is due to the proton in the —COOH group of the carboxylic acid. The two oxygens are both deshielding the H proton, which has resulted in a large chemical shift.

Intensity of the signal

The *intensity* of the signal shows the number of protons of that type. The area under the peak is proportional to the number of hydrogens in that environment. When the peak's bases are similar, the height of the peaks can be used as a ratio to calculate the number of protons in each environment. For ethane, there is only one peak. For ethanoic acid, there are two peaks with a ratio of 3:1. The peak corresponding to three protons in the methyl group has a peak area of 3 compared to the single proton on the —OH group. For ethanol, there are three peaks with a relative intensity of 3:2:1, as shown in Figure C8.27.



▼ **Figure C8.27** The high-resolution ^{1}H NMR spectrum of ethanol with the integration showing the ratio of the number of protons for each environment

WORKED EXAMPLE 8.2

Consider the molecule CH_3COH. Determine the:

a number of H environments.

b relative intensity of the peaks.

c expected chemical shifts.

Answers

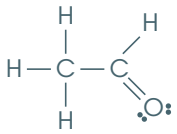
a There are two H environments.

b Relative intensity of the peaks is 3:1.

c CH_3 = 0.9 ppm, C(O)H = 9–10 ppm

Logic

1 Draw the structure.



2 Count the number of H on different atoms – check for symmetry.

There are two H environments in a ratio of 3:1.

3 From Table C8.4, the methyl would have a chemical shift near 0.9 ppm and the C(O)H group would be in the range of 9–10 ppm.

Try these yourself

a Determine the number of hydrogen environments and chemical shift for 1-butanol.

b Determine the number of hydrogen environments and chemical shift for the molecule on the right.

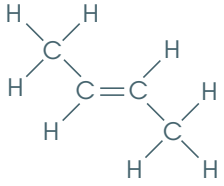




Figure C8.28 ▲
For one neighbouring proton, there are two possibilities: one aligned with and one aligned against.

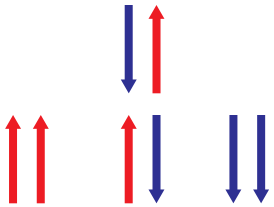


Figure C8.29 ▲
For two neighbouring protons, there are three possibilities: two protons aligned with, two against and one with and one against.

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1

Figure C8.30 ▲
Pascal's triangle

High-resolution ^{1}H NMR spectroscopy

High-resolution ^{1}H NMR spectroscopy can provide one additional piece of evidence compared to low-resolution ^{1}H NMR spectroscopy when determining the structure. The extra detail in the spectra shows the signal **splitting** into clusters of peaks. The splitting pattern shows the number of protons on adjacent atoms.

Neighbours: *n* + 1 rule

In ^{1}H NMR spectra, there is one more peak than there are hydrogens attached to the next atoms, the **neighbouring atoms**. In low-resolution ^{1}H NMR spectroscopy, a methyl group will have a chemical shift around 0.9 ppm, an integrated value of three and appear as a single line. In high-resolution ^{1}H NMR spectroscopy, the chemical shift and intensity will be the same but this peak may appear split. The common patterns observed are a doublet (two equal signals), a triplet (a set of three signals in the ratio of 1:2:1) and a quartet (a set of four signals in the ratio of 1:3:3:1). To work out the pattern, you have to count the number of protons on the adjacent atoms. The number of peaks can be calculated by using the $n + 1$ rule, where 'n' refers to the number of protons on the adjacent atoms.

Ethanol has a methyl group that will split into a triplet due to the —CH_2— group attached to the next carbon ($2 + 1 = 3$). The —CH_2— group will split into a quartet due to the methyl group ($3 + 1 = 4$). However, the peak due to the —OH group will remain a singlet despite two protons on the neighbouring carbon (Figure C8.27).

The splitting of the signal is due to **spin–spin coupling** with the neighbouring non-equivalent protons. The protons on the next carbon can be aligned with the proton (H atom) in the environment you are looking at and provide extra shielding. Or the neighbouring protons may align against the field and de-shield or shift the peak downfield. For one neighbouring proton, there are two possibilities: one with and one against (Figure C8.28). When there are two neighbouring protons, there are three possibilities: two protons aligned with, two against and one with and one against (Figure C8.29). Pascal's triangle can be used to determine the number and relative intensities of the peaks (Figure C8.30).

Table C8.5 Splitting pattern observed in high-resolution NMR

Neighbouring protons	Pattern		$n + 1$ =
0	Signal is not split	Singlet	1
1	Signal split into two	Doublet	1:1
2	Signal splits into three	Triplet	1:2:1
3	Signal splits into four	Quartet	1:3:3:1
4 or more		Multiplet	

No splitting!

There are a couple of times when you do not get a signal splitting. This occurs when the neighbouring nuclei has the same chemical shift or the proton belongs to an —OH group. There is no interaction between the H on the —OH group with any H on the neighbouring carbon. The proton does not cause splitting and never splits. The —OH group may vary its chemical shift depending on the conditions that the spectra are taken but it is always a singlet.

The splitting pattern is observed only in high-resolution ^{1}H NMR spectra. The (n + 1) rule can be used to determine the number of protons on adjacent atoms, the nearest neighbours.

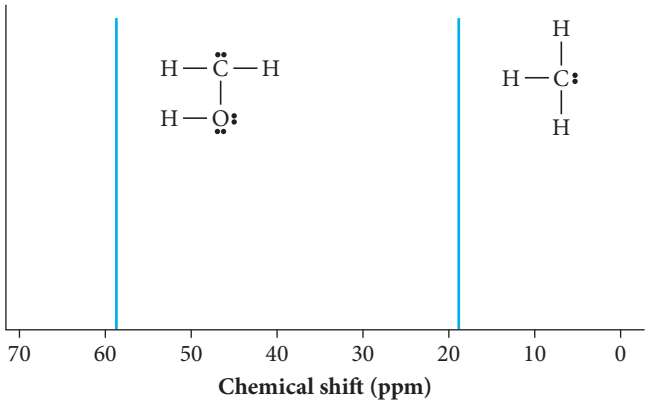
^{13}C NMR spectroscopy

The ^{13}C isotope is only about 1 per cent in abundance compared to the ^{12}C isotope. As such, ^{13}C NMR spectra take much longer and do not provide the same details as the ^{1}H NMR spectra.

^{13}C NMR spectra will indicate the number of different carbon environments by the number of different peaks observed. The type of carbon is indicated by the chemical shift of the peak. Due to peculiarities of the technique, the height does *not* relate to the number of carbons in each environment nor is splitting observed. The spectra are much simpler.

Table C8.6 Typical ^{13}C NMR carbon shifts values relative to TMS = 0. The solvent used may produce slightly different values, so these are a guide only

Type of carbon	Chemical shift (ppm)
R—CH_3	8–25
R—CH_2—R	20–45
R_3—CH	40–60
R_4—C	36–45
RCH_2—X	15–80
$RCNH_2$	35–70
RCH_2—OH	50–90
RC═CR	110–150
RCOOH	160–185



▲ **Figure C8.31** ^{13}C NMR spectrum of ethanol

ACTIVITY 8.2

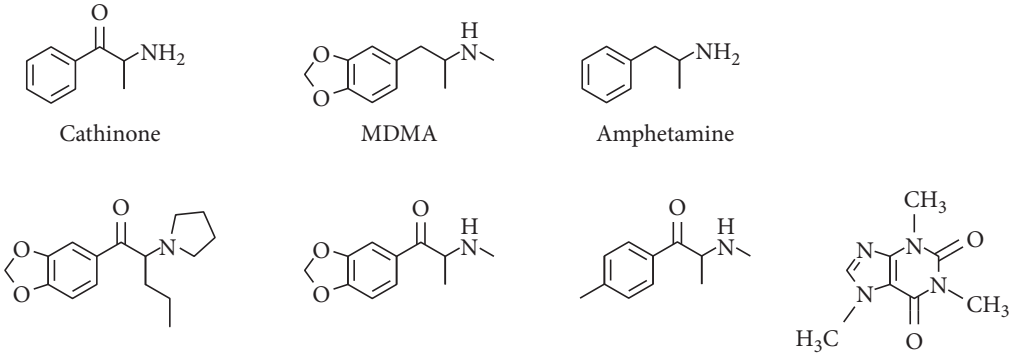
DETECTING DRUGS AND LIES

Aim

To determine whether ^{13}C NMR spectroscopy alone can detect the drug 'ecstacy' (3,4-methylene-dioxymethamphetamine, MDMA) from a range of other drugs

You will need

- Table of typical ^{13}C NMR values
- Computer with internet access

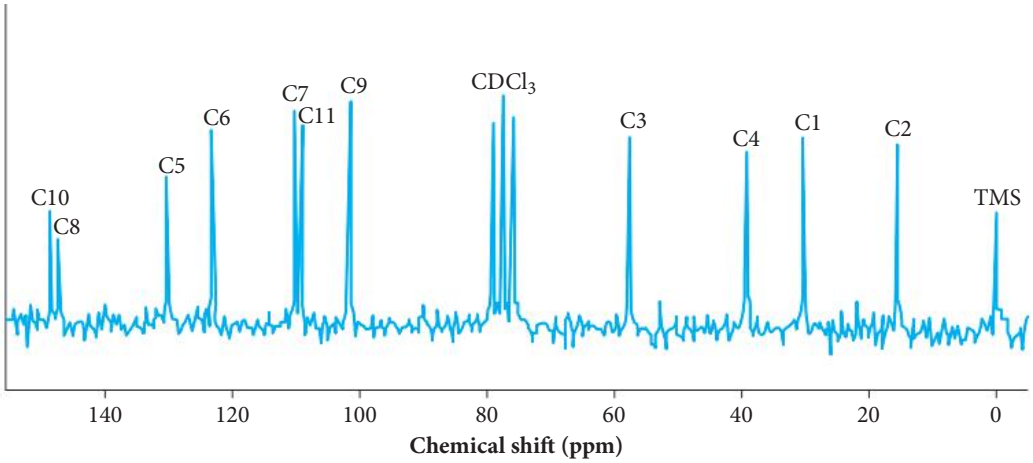


◀ **Figure C8.32**

What to do

1. Number the carbons on MDMA (Figure C8.32) to determine the number of different carbon environments.
2. Examine the other structures in Figure C8.32. Determine the number of different carbon environments for these molecules.

3 List the chemicals that could be present in a tablet of MDMA. Figure C8.33 shows the ^{13}C NMR spectrum of the confiscated pill thought to contain MDMA.



◀ **Figure C8.33**
^{13}C NMR spectrum of a pill that possibly contains MDMA

4 The purity of MDMA, 'ecstasy', is often less than 10 per cent. Caffeine is one of the common adulterants found in the pills. Could caffeine also be present in the sample?

5 Defences that have been used by criminals accused of operating clandestine laboratories include that the illegal drug was produced by accident, or that a fuel additive or perfume was the main target molecule. Research common perfume or fuel additive molecular structures.

What did you discover?

1 Why was ^{13}C NMR spectroscopy rather than ^{1}H NMR spectroscopy used in this case?
2 What technique would you suggest to separate the components of the pills?
3 Why would caffeine be a common adulterant used?
4 Why would the presence of other molecules lacing the pills be an issue?
5 Why is the defence that the target molecule was a perfume or fuel additive not likely to be supported.
6 Can ^{13}C NMR spectroscopy alone determine the presence of a drug such as MDMA in a sample? Explain.

QUESTION SET 8.3

Remembering

1 What two common isotopes are useful for NMR spectroscopy? Why are these able to be detected by NMR spectroscopy?
2 What part of the spectrum is used by NMR spectroscopy?
3 What are four things that can be determined by ^{1}H NMR spectroscopy?
4 What information does ^{13}C NMR spectroscopy provide?

Understanding

5 Predict the total number of peaks in the ^{1}H NMR and ^{13}C NMR spectra of the following compounds.
- a Methane
- b Ethane
- c Propan-2 -ol
- d Butanoic acid
- e Ethene
- f But-1-ene
- g But-2-ene
- h 1-Chloropentane
- i 3-Chloropentane

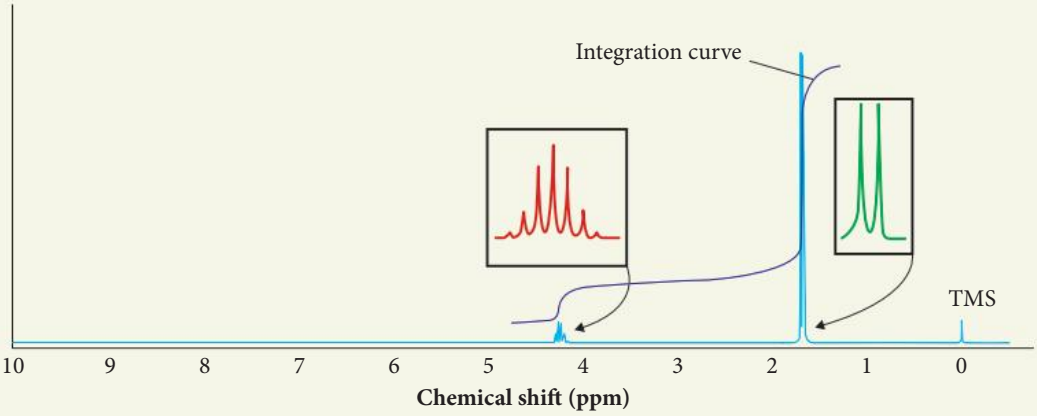
6 Provide explanations for:
- a the amount of energy needed for the nuclei to flip from a parallel to antiparallel alignment depends on the chemical environment.

b the splitting patterns (doublet, triplet, quartet) that occur in ^{1}H NMR spectroscopy.

c why CCl_4 is a common solvent for NMR spectroscopy.

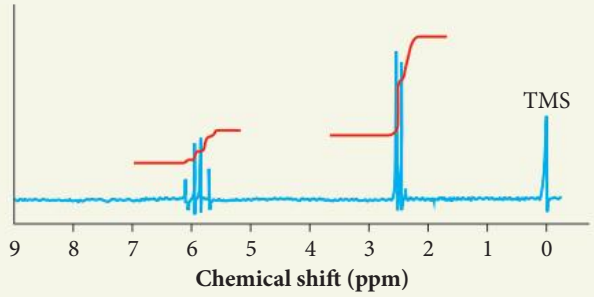
Applying

7 Account for all the peaks in the following ^{1}H NMR spectra for C_3H_7Br shown in Figure C8.34. What groups caused the observed splitting patterns? Determine the structure of the molecule.



◀ Figure C8.34

8 What is the structure of $C_2H_4Br_2$?



◀ Figure C8.35

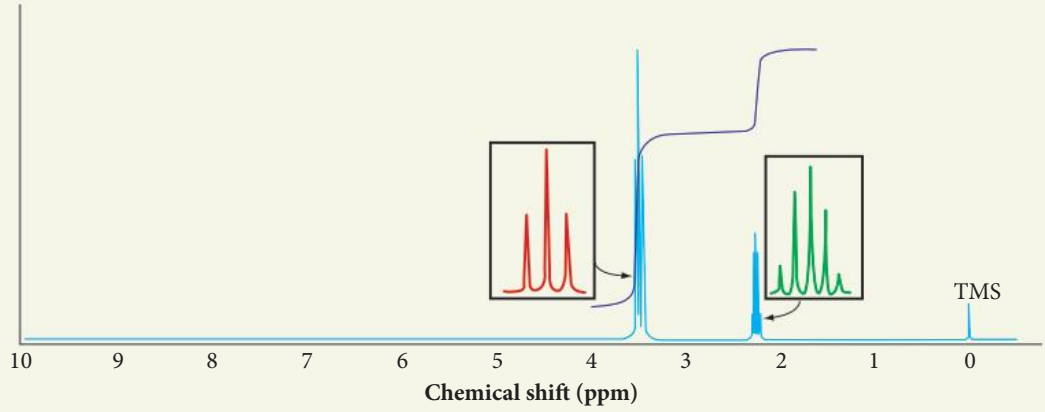
Analysing

9 Compound X contains C, H and Br. The chemical analysis shows that it contains 17.84% C and 79.19% Br. The mass spectrum showed the parent peak at *m/z* value of 200.

a Calculate the molecular formula of the compound.

b Why would you expect peaks at *m/z* 202 and 204?

c Examine Figure C8.36 and suggest a chemical structure for compound X.



◀ Figure C8.36

Reflecting

10 X-ray crystallography and NMR spectroscopy are both used for determining the structure of a biomolecule. In what ways do these techniques complement each other?

8.5 Infrared spectroscopy

Infrared spectroscopy is a useful technique for determining the bonds or functional groups that are present or absent in a compound. It is a relatively cheap and easy technique. It can be used in industrial applications for monitoring the chemical pathways, in forensic examinations and in drug development.

Principles of infrared spectroscopy

Molecules are constantly moving. The two basic modes of vibration are stretching and bending. A simple diatomic molecule is like two heavy spheres connected by a spring; the spheres can vibrate backwards and forwards around their equilibrium position, as shown in Figure C8.37a. In polyatomic molecules, such as water, the general vibration modes are shown in Figure C8.38a. The vibrations may be symmetrical or asymmetrical. A molecule can absorb infrared energy and change to higher energy vibration mode. The molecules will now vibrate with more energy and amplitude. The spring will be stretched to greater lengths and compressed more as shown in Figure C8.37b and C8.38b. When bending vibrations are excited, the change in angle is greater as shown in Figure C8.38b. This is not true for diatomic molecules such as O_2 and N_2; these molecules cannot be detected by infrared spectroscopy.

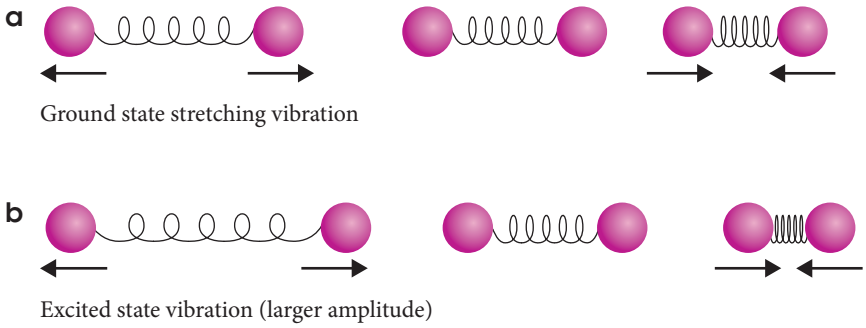


Figure C8.37 ▶ Vibrations for a) ground state and b) excited state of a diatomic molecule

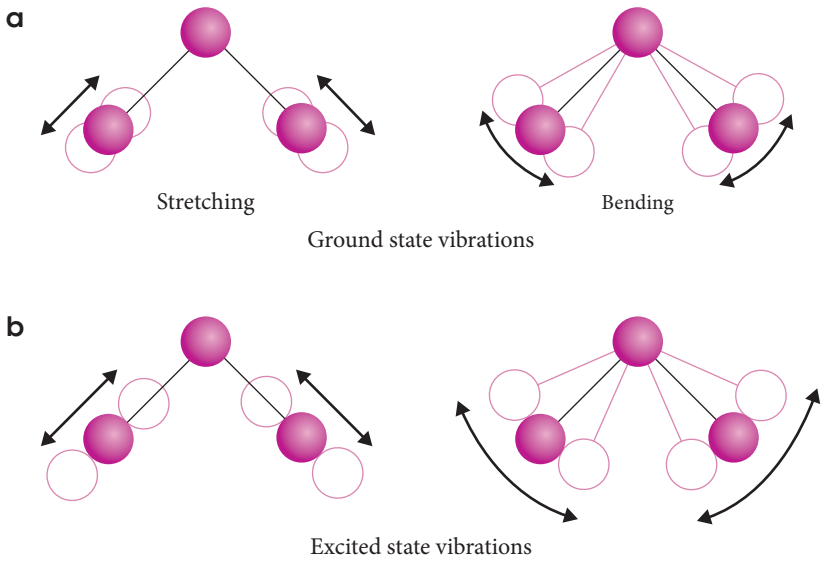


Figure C8.38 ▶ a) Ground and b) excited states of two of the vibrations that triatomic molecules undergo

The energy absorbed depends upon the bond length, the bond strength and the atom's size. Heavier atoms require more energy to increase vibration. Double bonds require more energy than single bonds to increase vibration. Measurement of the absorbance will determine which bonds are present. Typical absorbance values are shown in Table C8.7 on page 394.

A sample is placed in a cell that is in a beam of infrared radiation. A number of different frequencies is absorbed by the compound. The percentage transmitted is recorded against the energy of the frequency. The *x*-axis is the **wavenumber** (cm^{-1}), which is the inverse of wavelength (cm). The *x*-axis of the infrared spectrum always shows a dramatic change.

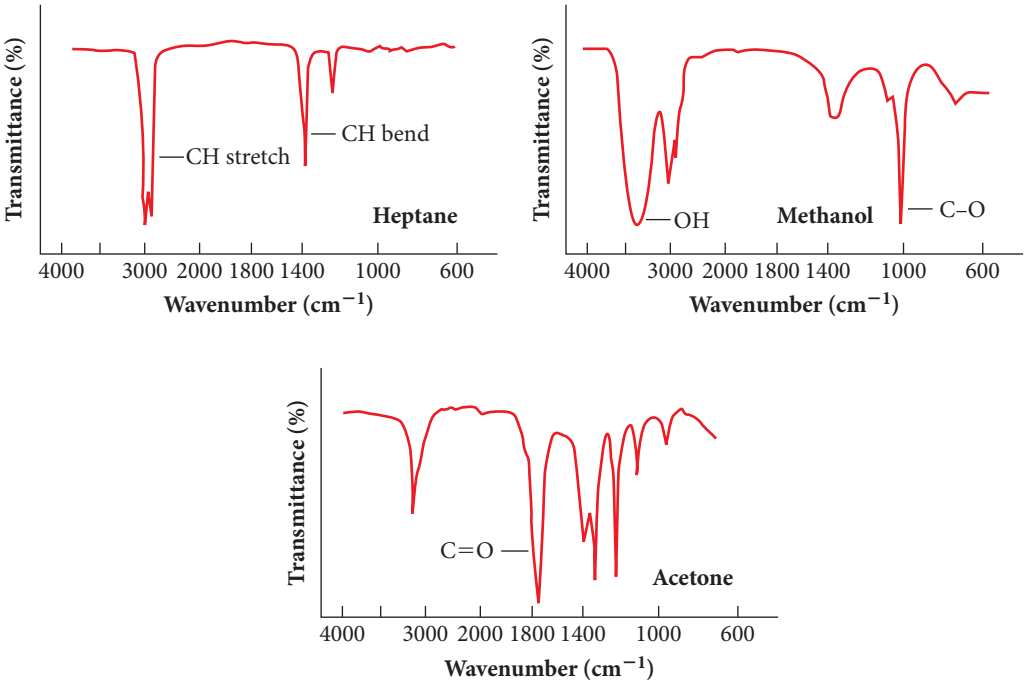
Unlike the earlier spectra, infrared spectra consist of a series of **troughs** from a base line; the spectra looks 'upside down'. The *y*-axis is the percentage of light transmitted. The base line shows 100 per cent of the light still being transmitted.

IR SPECTRA

Watch this video, which tells you how to run an IR spectrum.

Interpreting infrared spectra

To interpret infrared spectra, you look for key troughs or **absorption bands**. Infrared spectra consist of a large number of bands that are ignored when interpreting spectra because they are due to many different vibrational modes of the molecules that do not provide useful information. The key area to examine is in the higher wavenumber region. Notice in the spectra that the *x*-axis has a change of scale. The troughs to the right of around 1400 cm^{-1} are called the fingerprint region.



◀ **Figure C8.39** Infrared spectra of heptane, methanol and propanone (CH_3COCH_3). The broad trough at around 3200 cm^{-1} is characteristic of an alcohol –OH stretch. The vibrations that cause the major absorption bands are identified.

IR spectroscopy determines the presence or absence of functional groups. IR energy increases the vibration and bending of the molecule. The wavenumber is affected by the size of the atoms, bond length and strength.

Almost every organic molecule has a —C—H bond (where a hydrogen is attached to a carbon), which absorbs somewhere in the range from 2800–3000 cm^{-1}. This trough does not provide much information. Neither does the band due to a —C—C bond.

The —OH bond as found in alcohols typically absorbs at 3000–3500 cm^{-1}. This is usually broad and characteristic. The —C═O bond at 1700 cm^{-1} is also very useful. The presence of a broad trough at 3000 cm^{-1} could indicate that the compound is an alcohol. But when present with a band also at 1700 cm^{-1}, the compound could be a carboxylic acid.

Table C8.7 Characteristic infrared absorption frequencies of some common functional groups

Class of compound and bond	Band positions (cm^{-1})
Alkanes, alkyl groups	
C—H	2850–2960
Alkenes	
—CH	3020–3100
—C═C	1650–1670
Alkyl halides	
C—Cl	600–800
C—Br	500–600
C—I	500
Alcohols	
—OH	3400–3650 (strong, broad)
—C—O	1050–1150
Amines	
N—H	3310–3500
C—N	1030–1230
Carbonyl compounds (e.g. carboxylic acids, esters)	
C═O	1670–1780
Carboxylic acids	
—OH	2500–3100 (strong, broad)

WOW

Sweet melody of glucose

German researchers are using infrared laser light to devise a novel, non-invasive way to monitor the sugar levels in people with diabetes. Dr Werner Mäntele's team at Frankfurt's Institut für Biophysik, Johann Wolfgang Goethe-Universität, is investigating a technique where the infrared beam is applied externally to the skin. Glucose molecules absorb infrared radiation and create a measurable sound signature. Researchers can detect glucose in skin fluids in seconds. Dr Mäntele's team refers to this as 'the sweet melody of glucose'. The researchers are hoping that the painless alternative to pricking a finger and using test strips will be available to people with diabetes in three years and a portable device available soon after.

Spectra fingerprint region

The region less than around 1400 cm^{-1} is called the **fingerprint region** and is 'unique' to a compound. It can be used to confirm the identity of the unknown compound by comparing it to a known sample. It can also indicate whether the sample is pure if the fingerprint region of the sample matches that of a pure standard. The trough may be of different intensities due to the concentration differences between the two samples.

SPECTROSCOPY IN A SUITCASE

See how mass and infrared spectroscopy can be used to solve mysteries.

ACTIVITY 8.3

MATCHING STRUCTURES

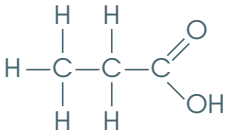
Aim

To identify structures from infrared and mass spectra data provided

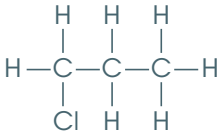
What to do

1. Examine the six molecules A–F and spectra 1–6.
2. Match the spectra to the organic molecules. (Hint: Calculate the molar mass.)
3. Look for possible common fragments.
4. Look for key functional groups in the infrared spectra.

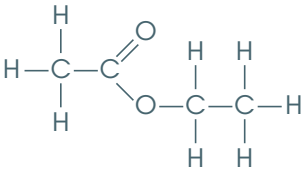
Molecule A



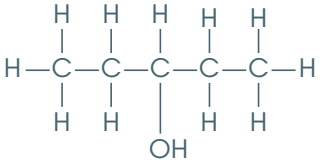
Molecule B



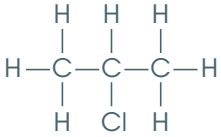
Molecule C



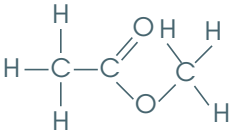
Molecule D



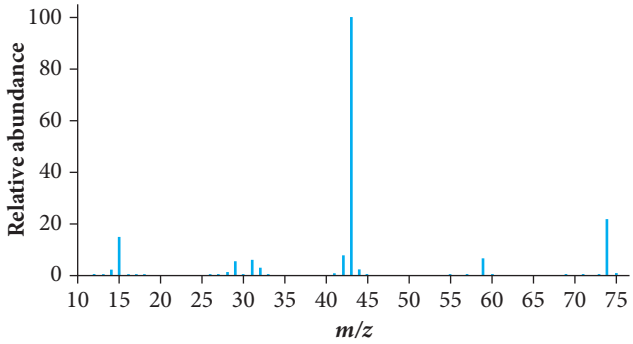
Molecule E

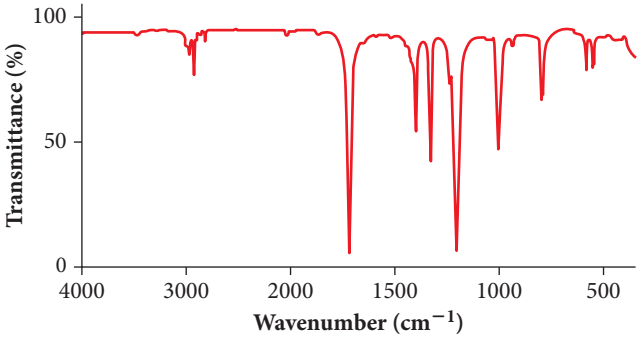


Molecule F

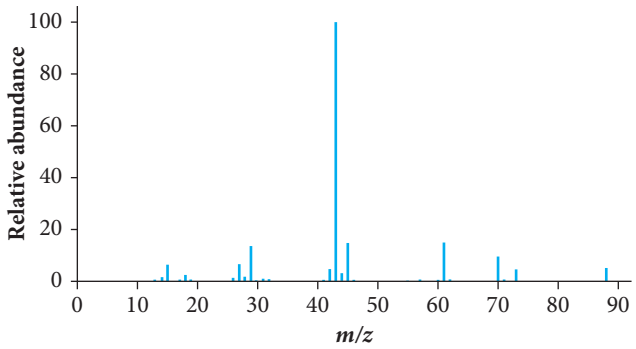


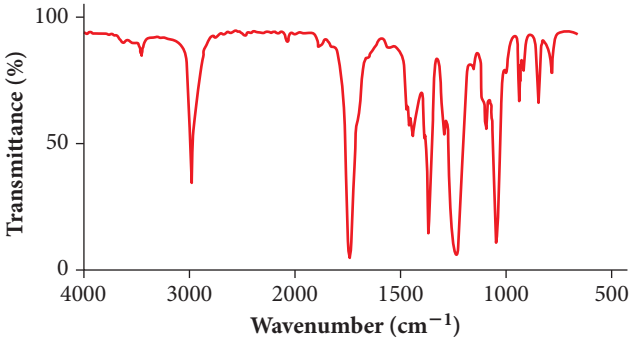
Spectra 1



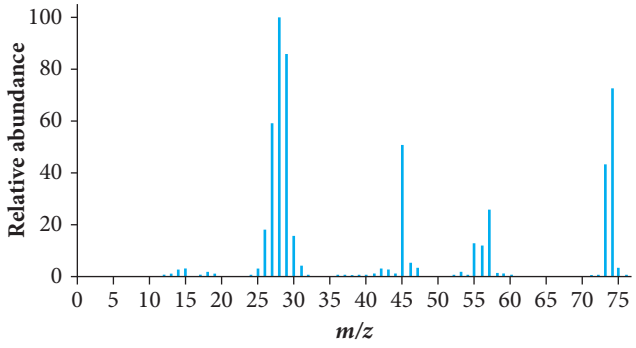


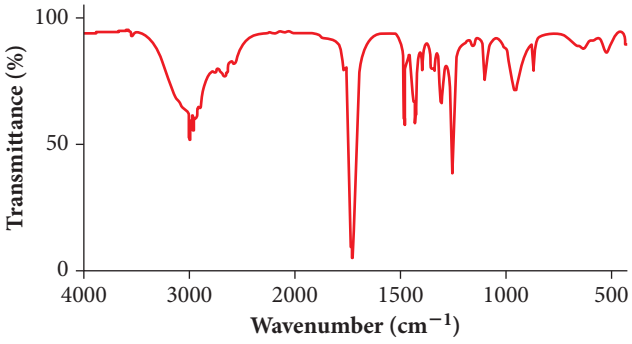
Spectra 2



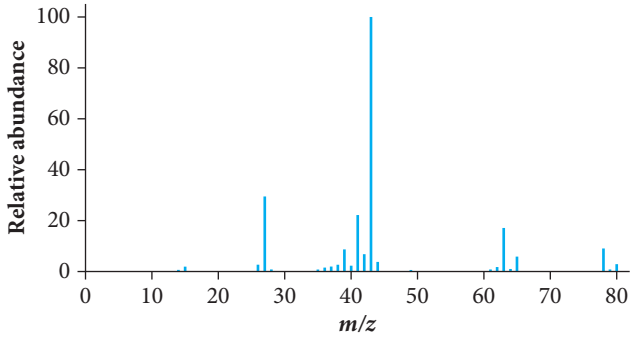


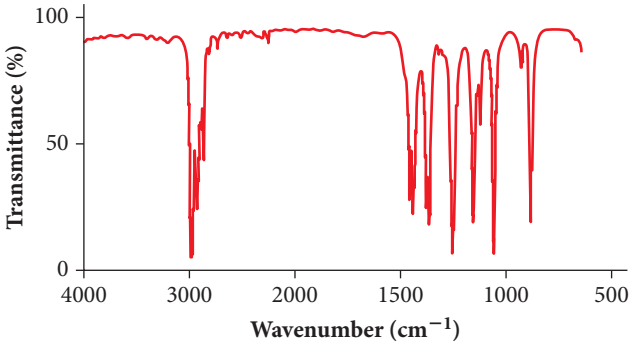
Spectra 3



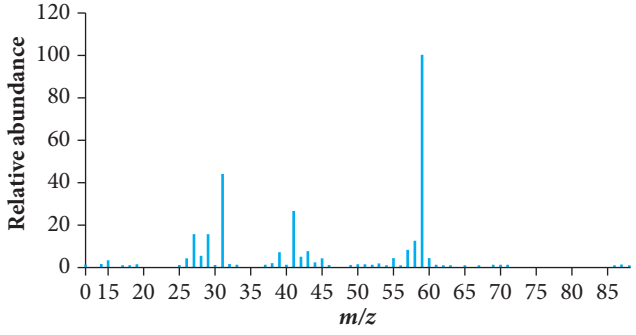


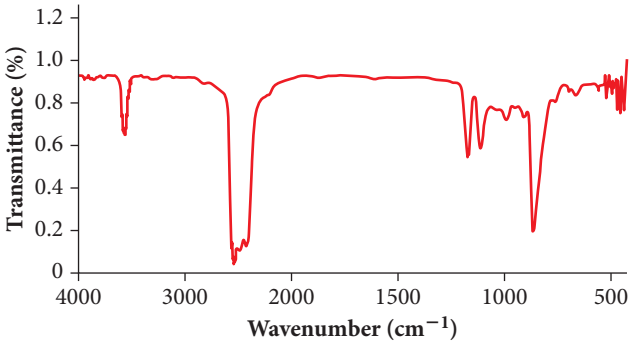
Spectra 4



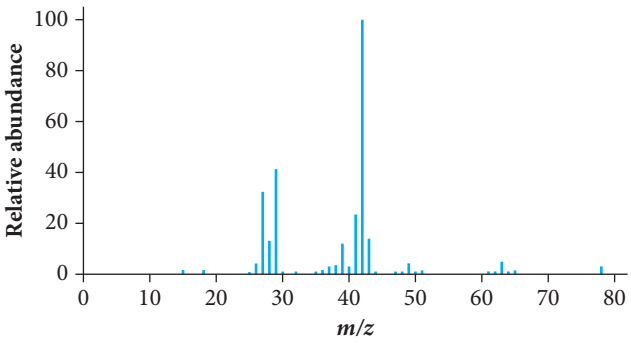


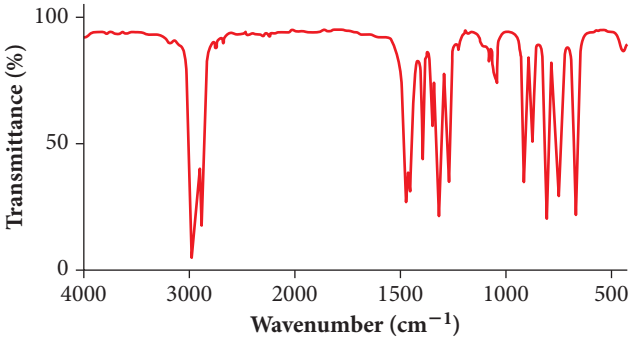
Spectra 5





Spectra 6





What did you discover?

1 What spectra belong to each compound?
2 Give the correct IUPAC name for each compound.

8.6 UV–visible spectroscopy

UV–visible spectroscopy is useful for determining the concentration of some organic molecules. The technique has been described earlier. It relies on the electrons in the molecules being excited to a higher energy state and uses the UV–visible part of the spectrum. It is usually the wavelength of light that gives the maximum absorbance that is chosen for analysis. This is an easy and relatively cheap technique.

UV–visible spectroscopy can be quantitative if a calibration curve is prepared using known concentrations of analyte. It is possible to confirm the identity of the substance by comparing the spectrum of a pure sample or standard of the compound.

ACTIVITY 8.4

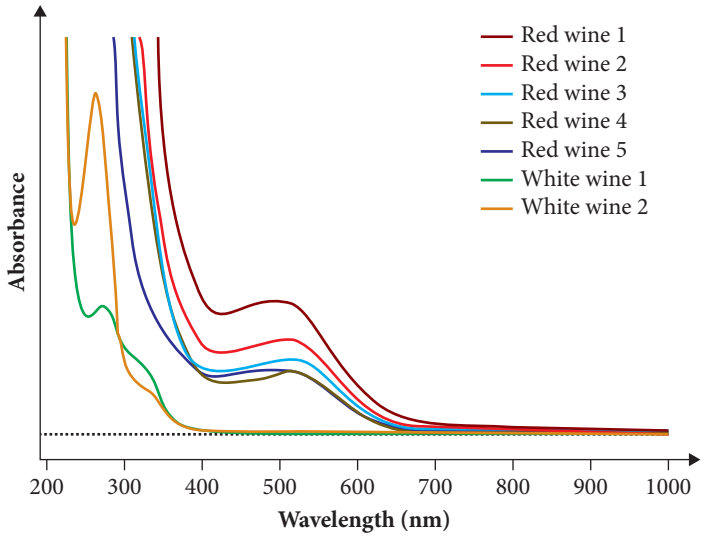
JUDGING WINE

Aim

To determine the wavelength for detecting phenolic compounds and determine which ones are more common in red than white wine

Table C8.8 Typical absorbance wavelengths for phenolic compounds

Phenolic compound	Typical wavelength (nm)
Anthocyanins	267–275, 475–54
Benzoic acids	235–305
Hydroxycinnamic acids	Absorbance maxima at 227–245 and 310–332
Flavonols	Typically have maxima at 250–270 and 350–390



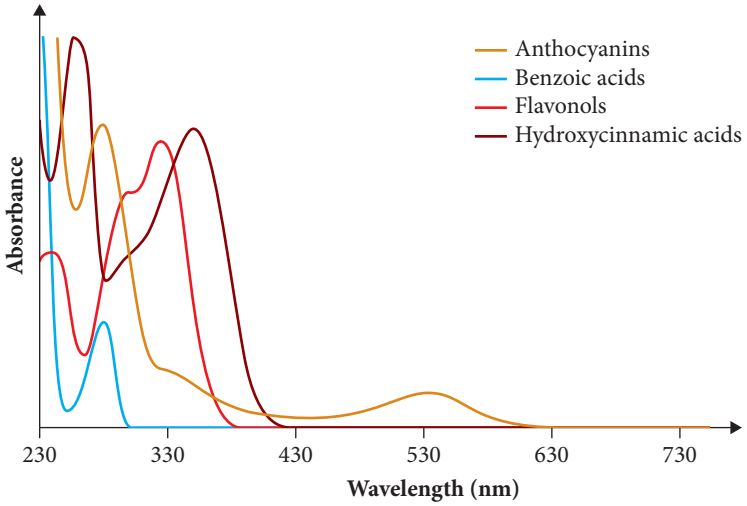
◀ **Figure C8.40** Absorbance spectra of wine samples

What to do

As a winemaker you need to judge the quality of the wine and be able to distinguish the different varieties. Phenolic compounds influence the colour and taste of the wine. It may be the grapes that cause the taste difference or it may be the treatment that allows the development of these different compounds

The winemaker ran UV–visible spectra of different wines as shown in Figure C8.40 and ran standard samples of the main phenolic compounds as shown in Figure C8.41.

Use these graphs and Table C8.8 to determine which phenolic compounds are common in red and white wine.



▲ **Figure C8.41** Absorbance spectra of main phenolic compounds found in wine

What did you discover?

1. Which specific wavelengths would you use to determine the different phenolic compounds? Justify your decisions.
2. Are the differences in the phenolic compounds in red or white wine?
3. Can these differences be determined by this technique using the provided data?

8.7 Combining techniques

Although a lot of information can be obtained by a single technique, much more information can be gained by combining them. Each technique provides one piece of the puzzle that is used to determine the whole structure. In 2002, the Nobel Prize in Chemistry was awarded for the development of a mass spectrometric analysis (John B. Fenn and Koichi Tanaka) and for the NMR development for biological macromolecules (Kurt Wüthrich). Their work determined the three-dimensional picture of what proteins look like in solution and enabled their function in the cell to be understood.

When you only have a small amount of sample, it is important to maximise the amount of information you can obtain from the techniques. The improved sensitivity of the instruments has meant that more information can be obtained. Precious artworks can be tested for

authenticity by gas chromatography, mass spectrometry and infrared spectroscopy – the pigments, glues and even the wooden frames can be analysed to determine if they originate from the era as well.

Manufacturers have now combined gas chromatographs and mass spectrometers into one instrument. A GC-MS is a gas chromatograph connected to a mass spectrometer. The GC separates the components and then they pass into a mass spectrometer. Here they are fragmented so that each component can have its structure unravelled.

Table C8.9 Typical analysis techniques for organic molecules

Technique	Main feature	What it does	Advantages	Disadvantages
NMR spectroscopy	Radio waves excite odd nuclei in a magnetic field.	Determines C—H backbone of organic molecules	Highly sensitive and precise Small sample size Sample can be in solution	Very expensive to buy and operate
X-ray diffractions	X-rays are scattered by crystals and result in a diffraction pattern.	Determines distances between the nuclei and the angles	Accurate and sensitive measurement of the distance between nuclei	Very expensive to buy and operate Crystals needed
Mass spectrometry	High-energy electrons produce cations, which are separated due to mass/charge.	Determines molar mass, isotopic abundances	Very sensitive Small sample size	Very expensive to buy and operate
Infrared spectroscopy	IR radiation increases the energy of the vibrational modes of the organic molecule.	Determines functional groups present	Huge range of analytes and samples small sample size	Moderately expensive
UV spectroscopy	Low molecular weight organic molecule's electrons are excited due to the absorption of UV light.	Can detect if a species is present Can be quantitative	Simple to operate	Not very sensitive
High-pressure liquid chromatography/ gas chromatography	Organic compounds are separated based on different adsorption and desorption rates between the mobile and the stationary phases.	Separates components	Relatively cheap	Specialist operators needed

QUESTION SET 8.4

Remembering

1 What technique would you use to determine the bonding groups in a compound?

2 What advantages are gained when techniques are combined?

3 What molecules cannot absorb infrared light?

4 Both UV–visible and infrared spectroscopy use part of the electromagnetic spectrum. What is similar to both techniques and what are two differences?

Understanding

5 Group the following compounds into those that would show or not show a broad peak at 3300 cm^{-1}: 1-propanol, 2-propanol, ethane, ethanol, ethanoic acid, methanoic (formic) acid, ethyl ethanoate, butanoic acid, 1-chloroethane, 1-methylamine.

Applying

6 Two compounds X and Y react with sulfuric acid to produce a compound that smells like nail polish remover (methyl ethanoate). A student tried to make this compound.

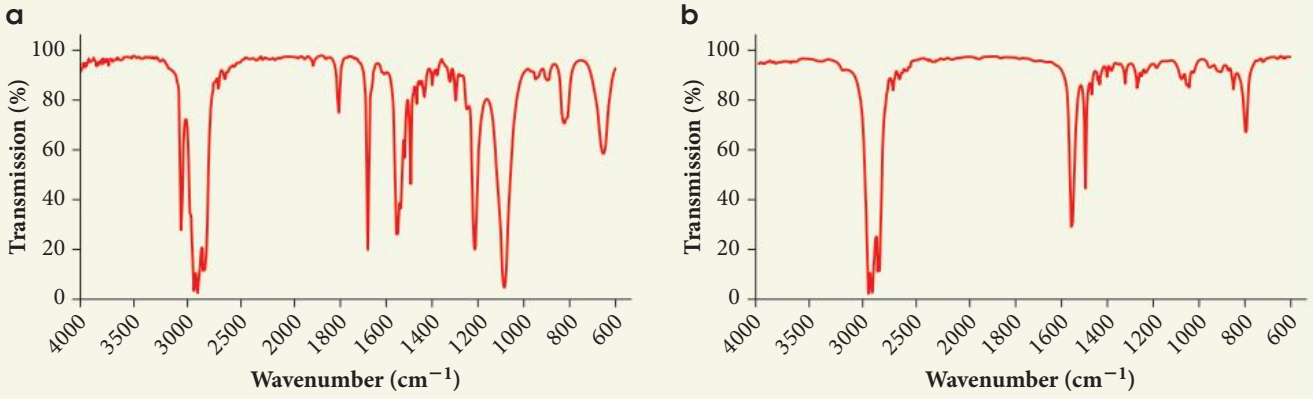
- a What would she see in the infrared spectrum to distinguish X and Y?
- b What would she see in the infrared spectrum for methyl ethanoate?
- c How would she be able to say that the sample is pure?

7 How could infrared spectroscopy be used to distinguish between the following pairs of compounds?

- a Ethane and ethene
- b Ethanol and propanol
- c 2-chloropropane and iodomethane
- d 1-propanol and propanoic acid

Analysing

8 Compare the two spectra in Figure C8.42. Assign each to either 1-hexene or hexane. Justify your decision. Account for the main absorption bands.



▲ Figure C8.42

CHAPTER CHECKLIST

You should know:

- how mass spectrometry produces cations, which are used to determine molar masses and isotopic abundances
- how ^{1}H NMR and ^{13}C NMR spectrometry are used to determine the different chemical environments within a molecule and the relative abundance of H in each environment, and how to use the $(n + 1)$ rule
- that IR spectroscopy will detect functional groups in organic molecules and UV–vis spectroscopy can detect some organic molecules.

You should be able to:

- interpret mass spectra, including simple fragmentation patterns, and distinguish between organic compounds with the same molar mass
- use tables to interpret NMR spectra, use this information to determine a molecule's carbon backbone and hence distinguish between different isomers
- interpret IR spectra by recognising key absorption bands, particularly the presence of —OH (alcohol), —OH (carboxylic acid) and —C═O bonds, and use this information to determine whether alcohols, esters or carboxylic acids are present, whether the substance is pure or whether a particular reaction has occurred
- recall the advantages and disadvantages of these techniques and determine when each one should be used and why some techniques are combined.

CHAPTER GLOSSARY

absorption band a trough observed at a particular wavenumber in infrared spectra

atomic mass unit (amu) the approximate mass of 1 nucleon; it is measured in a mass spectrum and carbon-12 is assigned an amu of 12

base peak the most common peak in a mass spectrum, it is assigned a value of 100% with other peaks relative to it

chemical shift (symbol δ (delta)) in NMR spectroscopy, it is the relative frequency that an odd nucleon nucleus will spin in a magnetic field compared to the standard tetramethylsilane (TMS), measured in ppm

diffraction the pattern seen in X-ray crystallography

fingerprint region area of IR spectrum characteristic for a particular substance; corresponds to a wavenumber less than 1400 cm^{-1}

isotope variant of an element that has a different number of neutrons; for example, carbon-12 and carbon-14

molecular ion (M^+) the largest peak (m/z) in a mass spectrum; generally corresponds to the molecular mass of the molecule

neighbouring atom the carbon or atom next to the atom holding the protons (hydrogen atoms) in question

nucleons a general name for both protons and neutrons

parent peak also called the molecular ion

radical a molecule with an unpaired electron; it is highly reactive

relative atomic mass (A_r) (RAM) the relative atomic mass of an element; the weighted average of the masses of the isotopes on a scale on which a carbon-12 atom has a mass of exactly 12 units

shielding the net effect of the electron shells and the neighbouring nuclei have on local electrical field felt by the proton or odd number nucleon

splitting the pattern seen in high-resolution NMR spectra due to the protons of the neighbouring atoms

spin–spin coupling the change in the local electrical field due to the presence of protons on the neighboring carbons

tetramethylsilane (TMS) the standard used in NMR spectroscopy that is considered to have a zero shift; the protons (hydrogen atoms) present have the maximum shielding

trough an absorption band in an IR spectra

wavenumber the inverse of wavelength; number of waves per centimetre; used in IR spectra

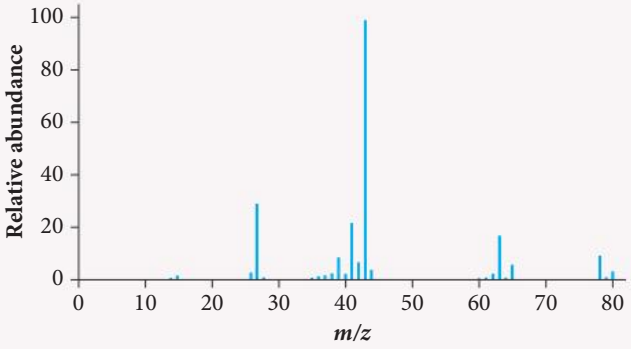
CHAPTER REVIEW QUESTIONS

Remembering

1 Which technique would be the easiest to use to distinguish carbohydrates, esters, carboxylic acids and amino acids?
2 What technique would be best to distinguish a range of carboxylic acids?
3 What information is given in an ^{1}H NMR spectrum. Why is NMR spectroscopy such a valuable technique for determining the structure of proteins and larger molecules?
4 Why do NMR spectroscopy and X-ray crystallography dominate the Noble Prize awards?
5 What technique is the best for determining the molar mass of a compound?
6 Why is the molar mass for an element given on the periodic table not a whole number?
7 What bonding is involved in the formation of crystals for X-ray crystallography?
8 What characteristic peaks would you expect in a mass spectrum of a choloroalkane?

Understanding

9 A compound was formed from the reaction of an alkene and HCl. The compound was 46% carbon and 9% hydrogen.
   a Determine the empirical formula for the compound.
   b Examine the mass spectrum (Figure C8.43) of the compound. What is the molecular formula for the compound?
   c Why is the parent peak not the peak with the largest *m/z* value in this case?
   d Draw the possible isomers for the compound.
   e Account for peaks at 43, 63 and 65.
   f Use the mass spectrum to decide which one is the most likely isomer.



◀ Figure C8.43

10 In court, criminals may claim that they were producing a perfume and not an illicit drug. How would infrared analysis help forensic scientists discredit the criminal? Would it be an advantage to take samples from the clandestine laboratory over time?
11 NMR and mass spectra can be used to determine the structures of molecules. How do these techniques differ in this task? Is just one of these sufficient?
12 How many peaks would be expected in a ^{1}H NMR spectrum for propanone (CH_3COCH_3)?
13 How could ^{1}H NMR spectroscopy be used to distinguish between 1-nitropropane and 2-nitropropane?
14 What differences would you expect in a mass spectrum of 1-chloropropane and 2-chloropropane?

Applying

15 Iodine has only one main stable isotope, ^{127}I. However, the treatment of thyroid cancer requires the following mixture of iodine isotopes: ^{123}I, ^{125}I and ^{131}I. These isotopes are produced in nuclear reactors and have a relatively short half-life: ^{131}I has a half-life of 8 days; ^{123}I has a half-life of 13 hours; and ^{125}I has a half-life of 60 days.
   a If the three isotopes were present in equal proportions, what would the RAM be when all three were produced?

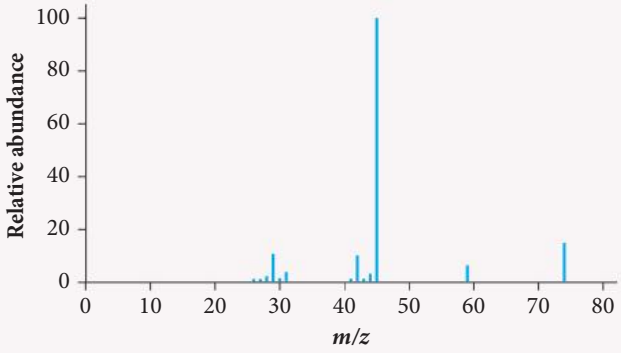
b Describe the changes expected in the RAM for the iodine at the end of 8 days.

c How would the mass spectrum of the iodine produced in the nuclear reaction differ from the standard mass spectrum for the element iodine?

16 X is an organic compound composed of carbon, hydrogen and oxygen. It contains 48.63% carbon and 8.18% hydrogen by mass.

a Calculate the empirical formula of X.

b The mass spectrum for X is shown in Figure C8.44.

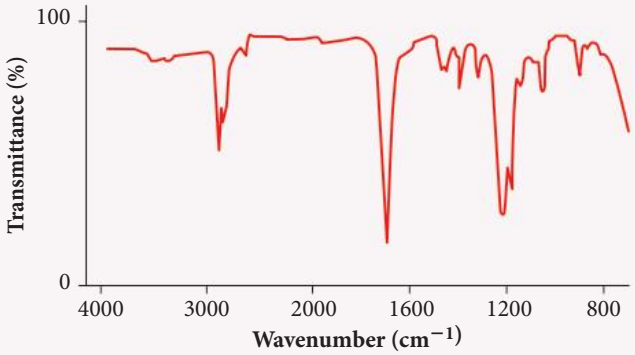


◀ **Figure C8.44** Mass spectrum of compound X

i Deduce, giving a reason, the molecular formula of X.

ii Identify the formulas of the fragment ions with *m/z* values of 45 and 29.

c The infrared spectrum of X is shown in Figure C8.45.



◀ **Figure C8.45** Infrared spectrum of compound X

i Explain why X is not a carboxylic acid.

ii Identify, giving reasons, three bonds that are present in X.

d Deduce the most likely structural formula of X based on your answers to parts **b** and **c**. State the name of X and give one use of compounds belonging to this homologous series.

e State and explain the number of peaks compound X will show in its low-resolution ^{1}H NMR spectrum.

f State the names of two compounds that could react together to produce X. Identify the type of reaction and give an equation for the reaction.

g Give structural formulas for two possible isomers of X.

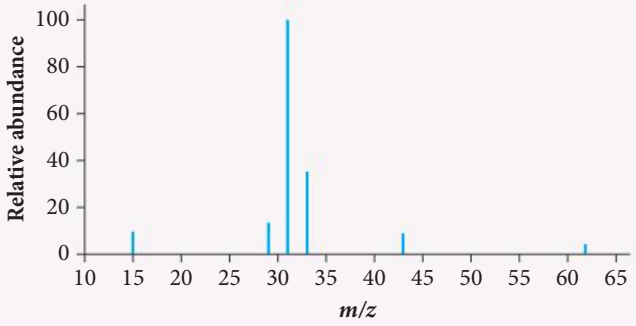
17 Proteins can be used as an early indicator or molecular marker for diseases such as cancer and heart disease. The cells in the body produce a different protein when under stress. How would you:

a separate these molecules?

b accurately determine their molecular mass?

c determine their molecular structure?

18 Assign the peaks for the mass spectrum in Figure C8.46. Is it 1,2-ethanediol? How many peaks would you expect in the low-resolution ^{1}H NMR spectrum?



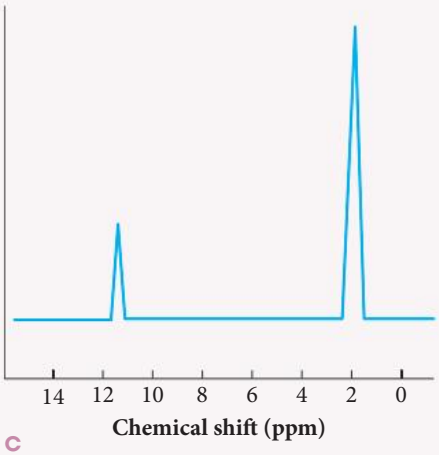
◀ **Figure C8.46** Mass spectrum

19 Salicyclic acid and acetic (ethanoic) anhydride react to form aspirin. This reaction does not go to completion. The salicyclic acid remaining will react with aqueous $FeCl_3$ to form a purple compound $FeCl_3$. How can the purity of the product be quantified by UV–visible or infrared spectroscopy?

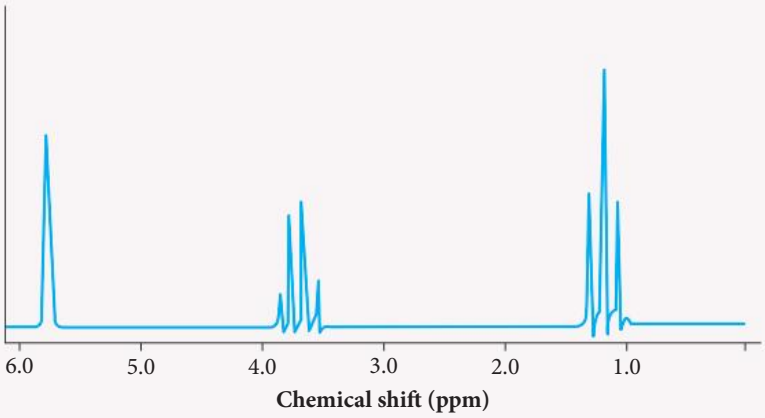
Analysing

20 Compare the following NMR, infrared and mass spectra. Assign each to ethanol, ethanoic acid or ethyl ethanoate.

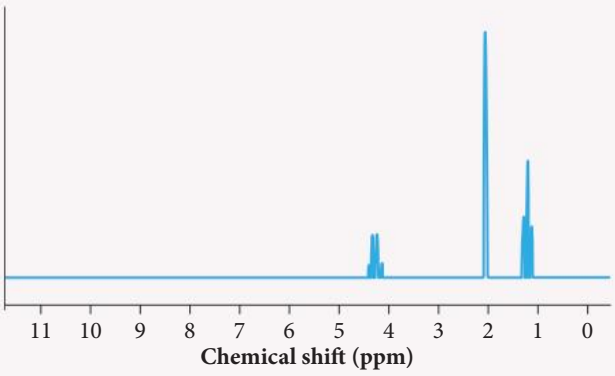
a



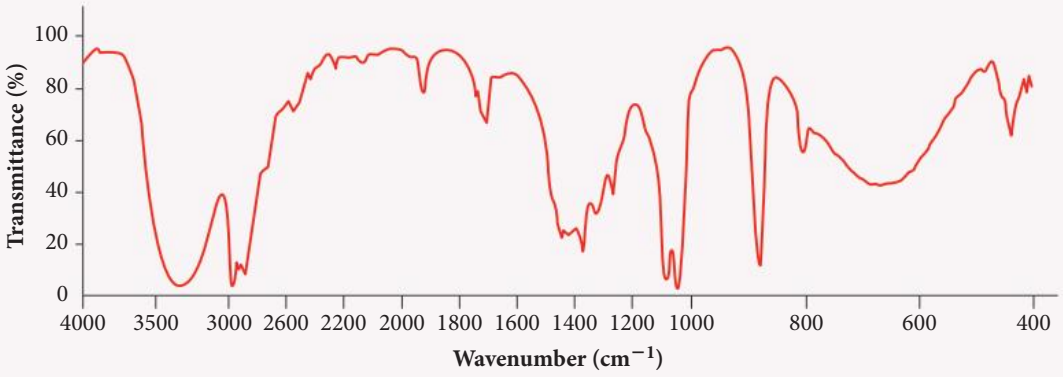
b



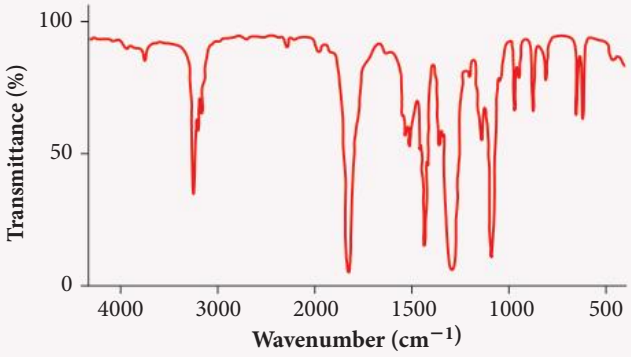
c



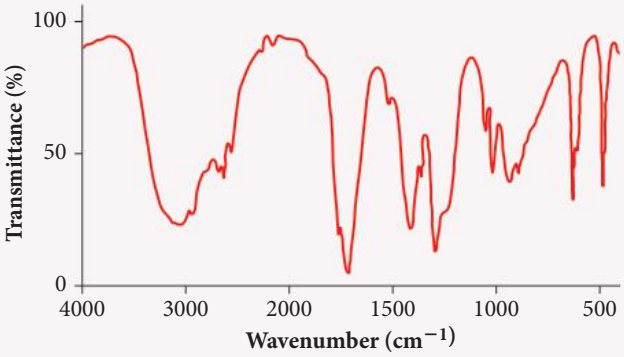
d


Transmittance (%)
100
80
60
40
20
0
4000 3500 3000 2600 2200 2000 1800 1600 1400 1200 1000 800 600 400
Wavenumber (cm^{-1})

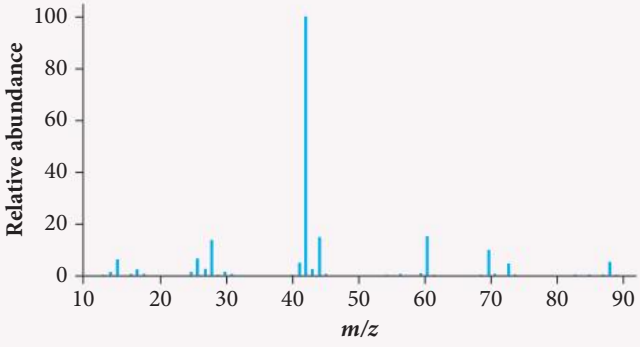
e


Transmittance (%)
100
50
0
4000 3000 2000 1500 1000 500
Wavenumber (cm^{-1})

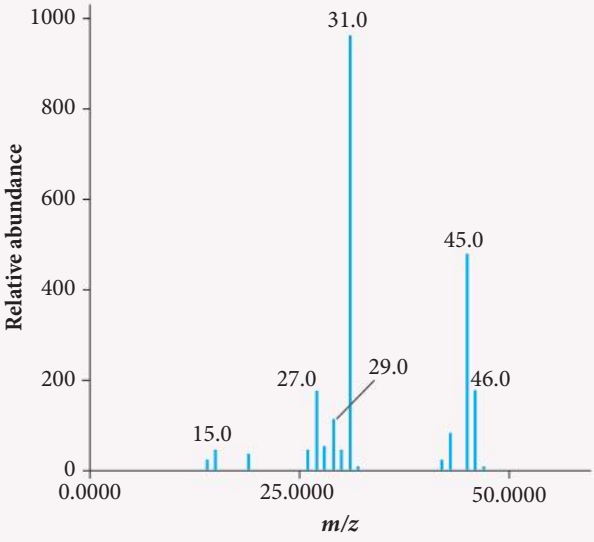
f


Transmittance (%)
100
50
0
4000 3000 2000 1500 1000 500
Wavenumber (cm^{-1})

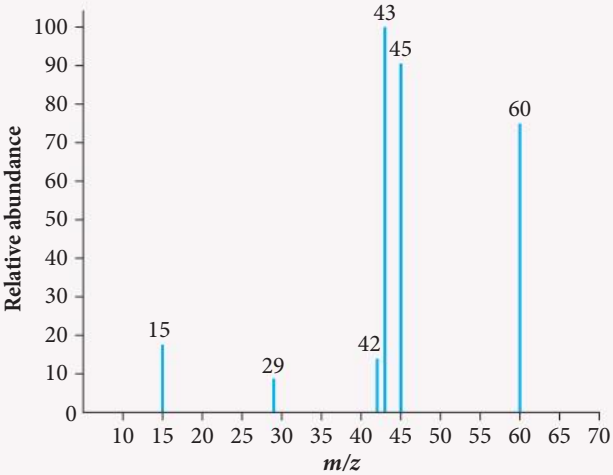
g


Relative abundance
100
80
60
40
20
0
10 20 30 40 50 60 70 80 90
m/z

h

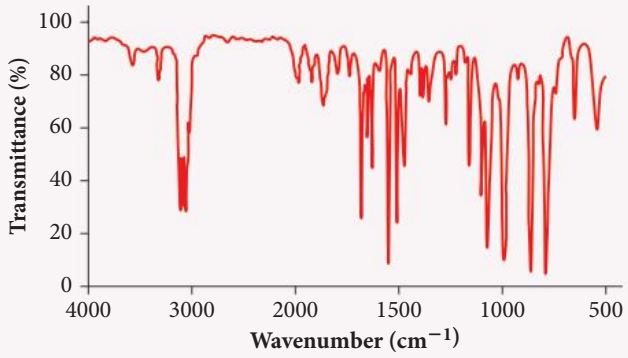

Relative abundance
1000
800
600
400
200
0
31.0
45.0
29.0
27.0
46.0
15.0
0.0000
25.0000
50.0000
m/z

i

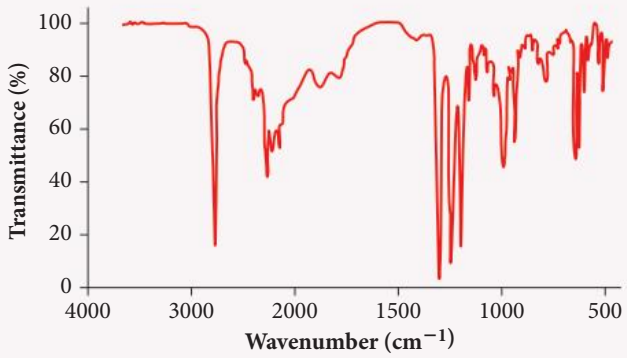

Relative abundance
100
90
80
70
60
50
40
30
20
10
0
43
45
60
15
29
42
10 15 20 25 30 35 40 45 50 55 60 65 70
m/z

21 A chemist had two different samples, A and B. Chemical testing found both samples had the same chemical composition: 54.55% C, 9.9% H, 10.7% N and the remainder oxygen.

A



B



a Calculate the empirical formula for sample A and B.

With the same empirical formula the chemist tried chemical reactions to tell them apart. Samples A and B both reacted with acids and bases.

b What is the likely biochemical group that sample A and B belong to?

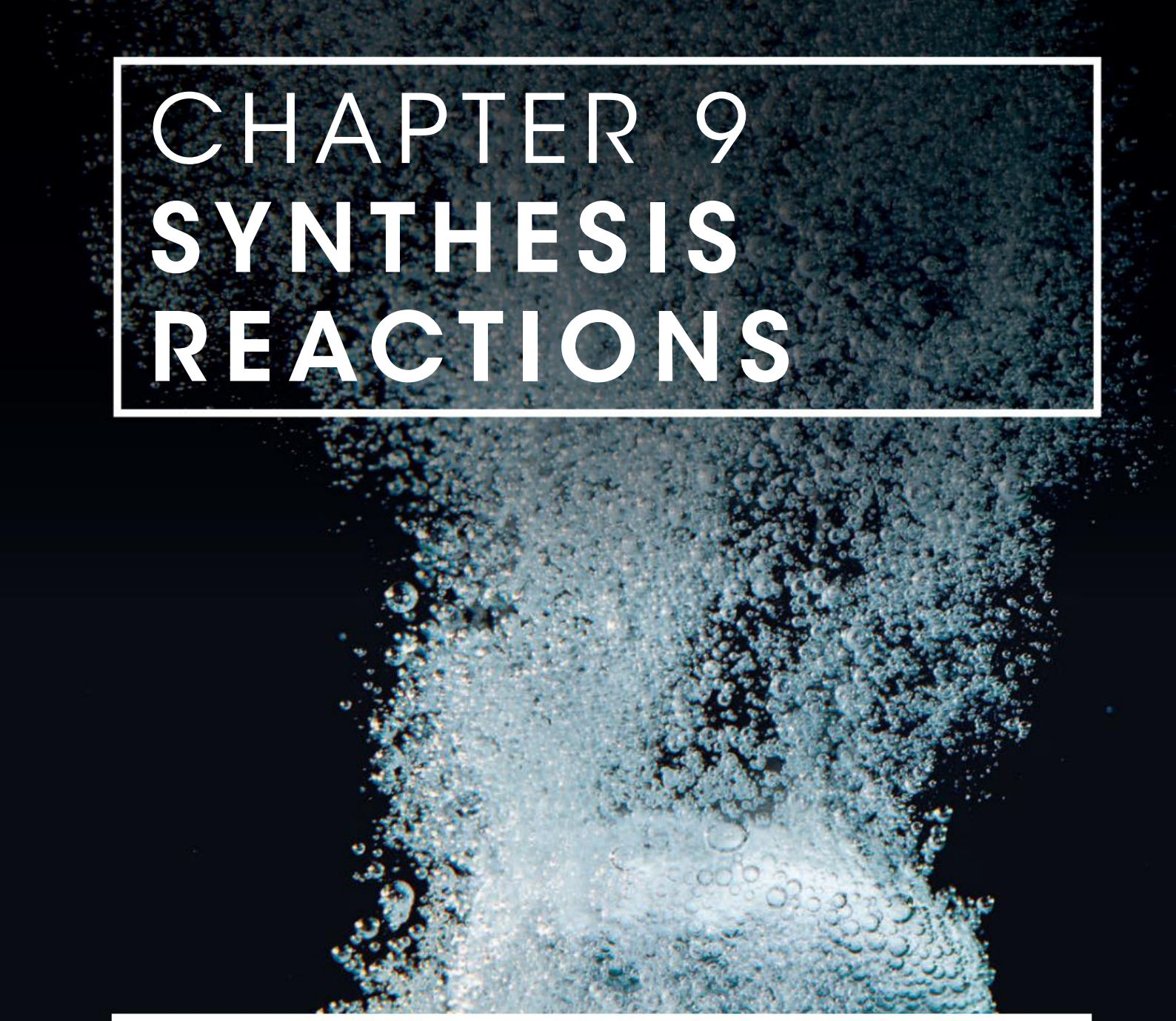
The chemist started to think that A and B were the same sample. So she ran infrared spectra on both and obtained the following spectra.

c Explain why the IR spectra confirm that they are *not* the same sample?

22 Aspirin is produced from the reaction of salicylic acid and ethanoic anhydride. Copy and complete the following table to show whether each technique is suitable for determining whether aspirin has been produced, evidence for the presence of aspirin and how you would use this technique to determine that the sample is pure.

Technique	Is technique suitable?	Evidence that would be present	How this technique could determine if sample was pure
IR spectroscopy			
NMR spectroscopy			
X-ray crystallography			
Mass spectrometry			
UV–vis spectroscopy			
HPLC/GC			

CHAPTER 9
SYNTHESIS REACTIONS



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By the end of this chapter you will have covered the following material.

Science Understanding

- Chemical synthesis involves the selection of particular reagents to form a product with specific properties (for example, pharmaceuticals, fuels, cosmetics, cleaning products) (ACSCH131)
- Designing chemical synthesis processes involves constructing reaction pathways that may include more than one chemical reaction (ACSCH132)
- Designing chemical synthesis processes includes identifying reagents and reaction conditions in order to maximise yield and purity of product (ACSCH133)
- The yield of a chemical synthesis reaction can be calculated by comparing stoichiometric quantities with actual quantities (ACSCH134)
- Green chemistry principles include the design of chemical synthesis processes that use renewable raw materials, limit the use of potentially harmful solvents and minimise the amount of unwanted products (ACSCH135)
- Fuel (for example, biodiesel, ethanol, hydrogen) can be synthesised from organic and inorganic sources using a range of chemical reactions, including addition, oxidation and esterification (ACSCH137)

9.1 Introduction

Can you imagine life without plastic? No plastic bags or PVC pipes, no plastic bottles or ice-cream containers. So many of the things we use every day are made from plastics. More specifically, they are made by chemistry being applied to make a new product. In other words, they are **synthesised**.

Plastics are not the only things that are synthesised. Many of the items that we rely on are manufactured by synthesis reactions. Pharmaceuticals, fuels, cosmetics and cleaning products are just a few examples.

Figure C9.1 ▶ What would we do without plastics? We have chemistry to thank for producing plastics for so many uses.



ZealPhotography/Alamy

9.2 Synthesis reactions

Chemical synthesis is very important. Aspirin, artificial sweetener aspartame, paint, plastic and soaps are just a few of the chemicals that we use every day. However, there are many factors to consider in the synthesis of a substance to ensure that the desired product is made in a cost-efficient, safe manner.

Figure C9.2 ▼ Aspirin tablets are synthesised by using chemistry.



Mark sykes/science photo library

In chemistry, synthesis is used to describe two different chemical reactions. The first involves two or more reactants combining to form a single product. For example, in the pop test, hydrogen and oxygen gas combine to form water:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

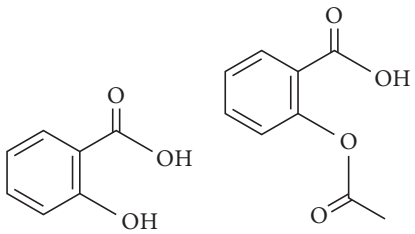
The second involves carrying out chemical reactions to purposely produce a specific product. It is this form of chemical synthesis that we will consider in more detail.

Uses of synthesis reactions

A huge variety of substances are produced by chemical synthesis, including pharmaceuticals, fuels, cosmetics and cleaning products. With each of these, a desired product is identified and then the reactants and **reaction pathway** are developed. In each case, the aim is to produce the product as economically and safely as possible with the least wastage.

Chemical synthesis involves choosing suitable reactants to form the desired product.

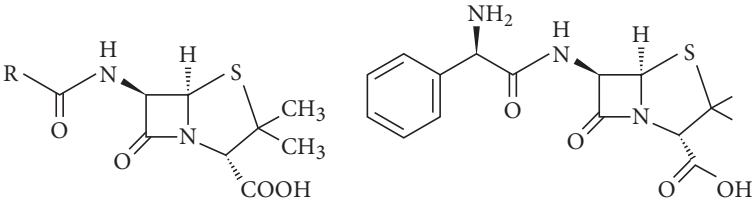
Aspirin is a pharmaceutical drug that is commonly used to alleviate pain and fever. Its use dates back centuries when people would eat ground-up willow bark to ease aches, pain and fever. The bark contains the compound salicin, which the body converts to salicylic acid. Unfortunately, salicylic acid can irritate the stomach. It was surmised that this side effect was due to the acidic nature of salicylic acid and scientists looked for a way of modifying the molecule to remove the acidic nature while maintaining the compound's activity. After much research and testing, it was found that changing salicylic acid to the ester acetylsalicylic acid achieved this effect. Aspirin is now manufactured on a huge scale utilising synthesis reactions.



Salicylic acid Acetylsalicylic acid

▲ **Figure C9.3** Salicylic acid and acetylsalicylic acid are compounds that are effective in relieving pain.

Penicillin is another pharmaceutical drug that is produced by synthesis reactions. Penicillin, discovered by Alexander Fleming in 1928, was collected originally from the *Penicillium* fungus. However, in 1948, John C. Sheehan started nine years of research into manufacturing synthetic penicillin. Although his method was not suitable for mass producing penicillin, one of the **intermediates** produced could be altered to form a variety of different forms of penicillin that are still used today, including ampicillin (Figure C9.4).



Penicillin Ampicillin

◀ **Figure C9.4** Structure of penicillin and ampicillin antibiotics, which are used to treat bacterial infections

9.3 Designing synthesis reactions

Scientists have known about synthesis reactions since 1828 when Friederich Wöhler tried to produce ammonium cyanate from silver cyanate. The reaction did not produce ammonium cyanate, but one of its isomers, urea. Twenty years later, scientists produced another organic compound, acetic acid, from inorganic reactants. This was followed by the synthesis of a greater range of organic compounds. Since then, the range of compounds able to be synthesised has grown, as has the range of techniques that are utilised.

WOW

Quinine synthesis

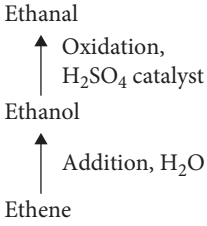
Quinine is an important drug for the treatment of malaria, and therefore is responsible for saving many lives. Its original source was the bark of the *Cinchona officinalis* tree from South America. A decrease in the number of these trees increased the price of quinine. In 1856, 18-year-old William Perkin attempted to synthesise quinine in his laboratory at home. Although he was not successful, it led to research into the necessary reaction, and 88 years later, R.B. Woodward and W.E. Doering finally achieved the synthesis of quinine.

Choosing the reactants

A common method of designing synthesis reactions is to start with the desired product and work backwards. This process is called **retrosynthetic analysis** and was developed by Professor E.J. Corey. Retrosynthetic analysis has changed the way organic compounds are synthesised and Corey was awarded the Nobel Prize in Chemistry in 1990.

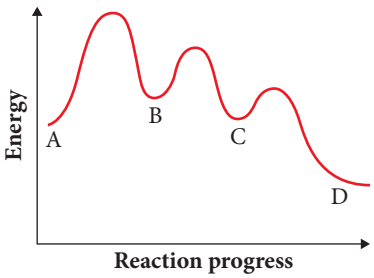
Many chemicals synthesised are organic compounds. In the synthesis of these compounds, the steps are identified by starting with the product and then gradually removing carbons or simplifying the compound until suitable reactants are identified.

For example, ethanal is an aldehyde with two carbons in the chain. This aldehyde can be made from ethanol – a primary alcohol with two carbons in the chain. This alcohol can be made from ethene. Therefore, in this case, the initial reactant would be ethene (Figure C9.5).



▲ **Figure C9.5** Retrosynthetic analysis for the production of ethanal

Choosing the reaction pathway



▲ Figure C9.6
Energy profile diagram for a multistep reaction

In most cases, the synthesis reaction involves more than one step. There are many factors to consider when deciding on the appropriate steps. These include other possible products, availability and cost of reactants and the conditions required for the reaction. Although there may be more than one possible pathway, or **reaction mechanism**, chemists choose the pathway that allows them to produce the product as cheaply, safely and efficiently as possible.

In a multistep reaction, each step will have its own reactants, products and activation energy. These will affect the speed of the reaction and the chemicals available for the next step. Along the pathway, the products of one step may be used as reactants for another step. Therefore, these products are used up during the process. These chemicals are known as intermediates. An energy profile diagram can be used to represent the stages of the reaction (Figure C9.6).

In Figure C9.6:

- A is a reactant
- B and C are intermediates
- D is a product.

When choosing the most appropriate steps, scientists will also consider any side reactions that may occur and take steps to prevent these happening. This will maximise the purity of the product.

For more information about methods used to control the purity of the product, refer to Chemistry section 10.1, page 432.

Reaction pathways for chemical synthesis may include more than one chemical reaction.

Multistep processes

The **contact process** is a method used to produce sulfuric acid. It involves a multistep reaction pathway. The steps have been chosen to allow the acid to be produced as efficiently and safely as possible.

The first step involves the production of sulfur dioxide through the **combustion** of either sulfur or sulfide ores such as iron(IV) sulfide:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

or

$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

In the second step, the sulfur dioxide reacts with oxygen to produce sulfur trioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The sulfur trioxide is then dissolved in concentrated sulfuric acid before reacting it with water to produce sulfuric acid:

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

For more information on esters, refer to Chemistry section 6.9, page 310.

Each step in the reaction mechanism has its own reactants and products, the product in one reaction being the reactant in the next. Therefore, sulfur dioxide and sulfur trioxide can be considered as intermediates in the overall reaction.

Another example of a multistep pathway is the production of ethyl ethanoate. In the first step, ethene reacts with steam to form ethanol:

$$CH_2CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$$

In the second step, ethanol reacts with acetic (ethanoic) acid to produce the ester ethyl ethanoate:

$$CH_3CH_2OH(g) + CH_3COOH(aq) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

The steps and the conditions under which reactions are carried out are chosen for a specific reason. We will consider the reason for the conditions in each step in the next section.

Linear or convergent pathways

The sequence of steps in the reaction mechanism is another factor that scientists must consider when designing synthesis reactions. The sequence may be either linear or convergent. A **linear sequence** has one reaction following the other, with the products of one reaction being used in the next reaction (Figure C9.7).

$$A \rightarrow B \rightarrow C \rightarrow D \rightarrow E \rightarrow F$$

◀ **Figure C9.7**
A linear synthesis sequence

The contact process on page 410 is an example of a linear sequence. The sulfur dioxide produced in the first reaction is used in the second reaction. The sulfur trioxide produced in this second reaction is then used in the third reaction. Then, the oleum ($H_2S_2O_7$) produced in the third reaction is used in the final reaction, which produces sulfuric acid.

$$S(s) + O_2(g) \rightarrow SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

◀ **Figure C9.8**
The contact process uses a linear sequence

A **convergent sequence** uses different reaction pathways and then the products from these are combined as reactants in another reaction (Figure C9.9).

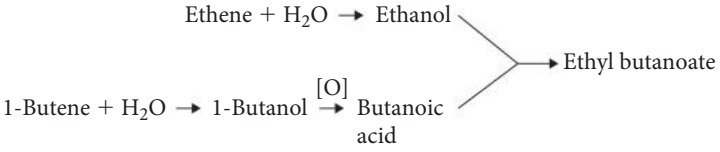
$$\left.\begin{array}{l} A \rightarrow B \rightarrow C \\ U \rightarrow V \rightarrow W \end{array}\right\} \rightarrow F$$

◀ **Figure C9.9**
A convergent synthesis sequence

The synthesis of an ester is an example of a convergent process. An ester is produced by the reaction of a carboxylic acid with a primary alcohol in the presence of an acid as a catalyst. Therefore, the synthesis of an ester would involve:

1 production of the appropriate carboxylic acid
2 production of the appropriate alcohol
3 reacting the carboxylic acid with the alcohol in the presence of an acid such as sulfuric acid.

The convergent process for the synthesis of ethyl butanoate can be represented by the flowchart in Figure C9.10. Ethyl butanoate is an ester with a banana odour.



◀ **Figure C9.10**
The convergent synthesis of ethyl butanoate; [O] represents an oxidation reaction.

For each synthesis, the individual reactions should be considered to determine the best pathway. However, if the efficiencies of the reactions are similar, then a convergent sequence would have a higher overall yield than a linear synthesis of the desired product.

To see applications of designing reactions, refer to Context 4, 'Polymer chemistry', page 102.

To learn about how to prevent unwanted reactions, refer to Chemistry section 10.4, page 448.

QUESTION SET 9.1

Remembering

1 List five substances that you commonly use that are produced through synthesis reactions.
2 List some factors that must be considered when choosing the steps in a reaction pathway.

Understanding

3 Explain the process of retrosynthetic analysis.
4 Explain why the contact process is considered a linear sequence.

Applying

5 Explain why it is important to choose the most suitable reactants and reaction pathways when designing a synthesis reaction.

9.4 Yields of reactions

In Chemistry section 1.3, you considered how equilibrium affected the **yield** of the reaction. These principles are also very important in synthesis reactions because they will determine whether the process is economically viable.

What is yield?

When we perform calculations in chemistry, we often assume that all the reactants will react to form the products. In reality, this does not always happen. The yield of a reaction refers to the amount of product actually produced from the reactants. A reaction with a high yield will produce a large amount of product from the reactants.

Maximising yield



To refresh your understanding of equilibrium, refer to Chemistry sections 1.3 and 1.4, pages 146 and 154.

In industry, it is desirable to make as much of the product as possible. To facilitate this, the conditions would be managed so that **equilibrium** lies as far to the right as possible. This means that at equilibrium, there will be a much higher proportion of products than reactants. This means that a high proportion of the reactants have become products. The conditions required will vary depending on the reaction; however, there are some common features.

- The removal of the product: By decreasing the concentration of a product the forward reaction will be favoured, shifting equilibrium to the right.
- Recycling of reactants that have not been used: By recycling the unused reactants, there is less wastage. It also increases the concentration of a reactant. This favours the forward reaction, shifting equilibrium to the right.
- Conducting the reaction at an appropriate temperature: The temperature chosen should favour the forward reaction so that equilibrium lies as far to the right as possible. At the same time, the effect on the rate of the reaction and the cost of heating should be considered.
- Choosing a suitable pressure for a system including gases: The pressure of a gaseous system will affect the position of equilibrium; therefore, the pressure used should favour the forward reaction so that equilibrium lies as far to the right as possible. However, the effect on the rate of the reaction, cost and safety should also be considered.
- The addition of a catalyst is often used to increase the rate of production of the product. While this doesn't increase the yield, it will mean that the product is produced in a shorter time.

When designing the reaction conditions, the rate at which the yield is produced must also be considered. In an ideal situation, the reaction would have a high yield and this would be produced at a fast rate. That way a large amount of product is produced in a short time, thus maximising profit and minimising wastage. However, a compromise must often be reached between the yield and rate of the reaction when the one condition has opposite effects on the yield and rate.

Revise reaction rates by revisiting Nelson Chemistry Units 1 & 2 for the Australian Curriculum, *Chapter 9.*

The contact process – understanding the conditions used

The contact process is used to produce sulfuric acid. It starts with sulfur or a sulfide, which undergoes a number of reactions to produce the acid.

Step 1 $S(s) + O_2(g) \rightarrow SO_2(g)$

or

$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$

Step 2 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Step 3 $SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$

$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$

In the first step, air is used as the source of oxygen. This is cheap and readily available. An excess of air is used, which provides the oxygen needed for the second step as well. This makes the process more efficient as the two reactants for the second step are already mixed together. However, the amount of air is controlled so that the ratio of sulfur dioxide to oxygen is 1:1.



CONTACT PROCESS

For more information about the contact process, visit this website.

From the equation for the second step, you can see that the stoichiometric ratio of the two reactants is $2SO_2 : 1O_2$. Therefore, the 1:1 ratio provided gives an excess of oxygen gas. This has the combined effect of increasing the reaction rate and increasing the yield of sulfur trioxide. The reaction rate is increased due to the increased concentration of the reactant, thereby increasing the number of collisions between reactant particles. By increasing the concentration of a reactant, the rate of the forward reaction will increase due to the increased number of collisions. This will shift equilibrium to the right and therefore increase the yield of sulfur trioxide.

The combustion of sulfur dioxide in the second step is an **exothermic reaction** with a **heat of reaction** of $-196\,kJ\,mol^{-1}$. An increase in temperature would lead to an increase in the rate of reaction due to the increased percentage of particles with enough energy for a successful collision. However, an increase in temperature would favour the **endothermic reaction**, which in this case is the reverse reaction. This would lead to a decreased yield of sulfur trioxide. Therefore, a compromise temperature of 400–450°C is used. This allows a relatively high yield of sulfur trioxide to be produced in a relatively short time.

The pressure of the chamber for the second reaction is 1–2 atm. A higher pressure would increase both the rate of the reaction and the yield of sulfur trioxide. The rate of the reaction would increase due to the increased concentration of the reactants and therefore the number of collisions between the particles. As there are more gaseous molecules in the reactants than the products, an increased pressure will increase the rate of the forward reaction more than the reverse. Therefore, equilibrium will shift to the right, increasing the yield of sulfur trioxide. However, it is very expensive to produce and maintain a high pressure safely; this cost outweighs the benefits gained. Therefore, a lower pressure is used.

The aim of the process is to produce as much sulfuric acid as quickly as possible. For this reason, a catalyst of vanadium oxide (V_2O_5) is used in the second step. Although this does not affect the yield of sulfur trioxide, it will increase the rate at which it is produced, thereby increasing the rate that the next step is able to proceed at.

If we consider the last two steps, it would seem counterproductive to add sulfuric acid when this is the desired product. If water was added directly to the sulfur trioxide, then sulfuric acid would be produced. However, this reaction is uncontrollable and will produce a fog of sulfuric acid. By dissolving the sulfur trioxide in the sulfuric acid first, the reaction can be controlled and the sulfuric acid produced can be collected efficiently. When we consider the molecules of sulfuric acid added and produced, it is clear that all of the sulfuric acid added is retrieved in the products in addition to the new sulfuric acid produced.

Designing chemical synthetic processes involves choosing reactants and conditions to maximise yield.

The Haber process – a compromise between yield and rate

The **Haber process** is used in the production of ammonia from nitrogen and hydrogen gas:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4\,kJ\,mol^{-1}$$

As with most industrial syntheses, the aim is to maximise the amount of ammonia produced in a given time at the lowest cost. Conditions are chosen that maximise the yield and rate while being cost efficient.

Revise the Haber process in Nelson Chemistry Units 1 & 2 for the Australian Curriculum, *Context 2 and Chapter 9.*

Temperature

Increasing the temperature will increase the rate of the reaction because more particles will have sufficient energy for a successful collision.

Decreasing the temperature will increase the yield because decreasing the temperature favours the exothermic reaction. In the Haber process, the exothermic reaction is the forward reaction; therefore, decreasing the temperature will increase the yield of ammonia.

Cost must also be considered. It is very expensive to heat chemicals to extreme temperatures and so any benefits may be offset by the cost.

HABER PROCESS

For more information about the Haber process, visit this website.

Therefore, a compromise is made between rate, yield and cost. A temperature of 400–450°C ensures that enough ammonia is produced in an adequate time.

Pressure

The rate of the reaction is increased by increasing the pressure of the system because this increases the concentration of the reactants and therefore the number of collisions.

Yield is also increased by increasing the pressure. Higher pressures favour the reaction that produces the least number of gaseous molecules. In the Haber process, this is the forward reaction and therefore the yield of ammonia is increased.

Although a higher pressure increases both the yield and rate, extreme pressures have associated risks and cost. It is very expensive to produce and maintain a very high pressure. There is also the risk of explosions if the pressure is greater than the container can withstand.

A pressure of approximately 200 atm provides a balance between the high rate and yield and cost and risks associated with even higher pressures.

Catalysts

Catalysts do not affect the yield of the reaction, but they can affect the rate. In the Haber process, an iron/iron oxide catalyst is used with a small amount of potassium oxide and aluminium oxide. This provides an alternative pathway for the reaction with a lower activation energy. Therefore, more particles will have sufficient energy for a successful collision.

Enzymes are biological catalysts. They are proteins whose properties, including shape, allow them to interact with the reactants of a reaction so that it is easier for the reaction to occur. This increases the rate of the reaction, in many cases making the reaction occur at a viable rate.

We can also use enzymes in industry to catalyse reactions. For some reactions, the temperature and pressure required for an adequate rate would be uneconomical. For others, the yield at high temperatures or pressures may be too low and so lower temperatures or pressures are used despite the lower reaction rate. The addition of a catalyst can allow the reaction to proceed at a higher rate despite the lower temperature and/or pressure.

The use of enzymes in the production of biodiesel and ethanol is further explored on page 423.

To see how better catalysts can be made, refer to Context 6, 'Molecular manufacturing', page 138.

Synthesis reactions are chosen to maximise the yield and purity of the product.

Calculating the theoretical yield – limiting reactants

The theoretical yield is the amount of product that can theoretically be produced from the reactants. It is based on the assumption that the reactants react with 100 per cent efficiency. In reality, many factors affect how much product is produced. One of these is the amounts of each reactant. As soon as one reactant runs out, the reaction can no longer proceed and no more product can be made. This reactant is known as the **limiting reactant** or **limiting reagent**. The other reactants are the **excess reactants** or **reagents**.

There are many different methods for determining which chemical is the limiting reactant. In each case, the number of moles of each reactant is compared to the stoichiometrical ratios needed in the reaction. One method is demonstrated in Worked example 9.1.

Once the limiting reactant has been determined, it is used to calculate the number of moles, and then the mass, volume or concentration of the product.

WORKED EXAMPLE 9.1

The synthesis of paracetamol ($C_8H_9NO_2$) is a three-step process with the final step being the reaction between *p*-aminophenol (C_6H_7NO) and ethanoic anhydride ($C_4H_6O_3$):

$$C_6H_7NO + C_4H_6O_3 \rightarrow C_8H_9NO_2 + C_2H_4O_2$$

If 0.5 g of *p*-aminophenol reacts with 0.4 g of ethanoic anhydride, what mass of paracetamol can be produced?

Answer

Mass of paracetamol is 0.593 g.

Logic

1 Calculate the number of moles of each reactant.

$$n = \frac{m}{M}$$

$$n(C_6H_7NO) = \frac{0.5}{109.1} = 0.00458\,\text{mol}$$

$$n(C_4H_6O_3) = \frac{0.4}{102.1} = 0.00392\,\text{mol}$$

2 Determine the stoichiometric ratio (SR), using the coefficients from the equation, and actual ratio (AR), using the moles calculated. Make sure that the same reactant is on top for both ratios.

$$\text{SR} = \frac{1}{1} = 1$$

$$\text{AR} = \frac{0.00458}{0.00392} = 1.168$$

3 Determine which reactant is limiting. If AR > SR, the reactant on the bottom is limiting. If SR > AR, the reactant on the top in limiting.

AR > SR, so the reactant in the denominator is limiting. Therefore, $C_4H_6O_3$ is limiting.

4 Use the moles of the limiting reactant to calculate the number of moles of the product that can be produced.

$$n(C_8H_9NO_2) = n(C_4H_6O_3)$$

$$n(C_8H_9NO_2) = 0.00392\,\text{mol}$$

5 Use the number of moles of the product to calculate the mass of the product that can be produced.

$$m = nM$$

$$m(C_8H_9NO_2) = 0.00392 \times 151.163 = 0.593\,\text{g}$$

Try these yourself

a What mass of ammonia can be produced from 5.0 L of hydrogen gas and 3.0 L of nitrogen gas at STP?

b What mass of sulfur trioxide can be produced from 1 kg of sulfur dioxide and 1 kg of oxygen gas?

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

Calculating percentage yield

The yield of a chemical synthesis can be calculated by comparing the stoichiometric quantities with the actual quantities.

The yield is usually given as a percentage of the possible yield. A yield of 90 per cent means that only 90 per cent of the amount of products that can be theoretically produced from the reactants is produced. To calculate this percentage we need to:

- use stoichiometry to calculate the amount of product that can theoretically be produced from the reactants
- know the amount of product actually produced.

Then calculate the **percentage yield**:

$$\text{Percentage yield} = \frac{\text{actual mass}}{\text{theoretical mass}} \times 100$$

PERCENTAGE YIELD

For more information about percentage yield, visit this website.

WORKED EXAMPLE 9.2

If 5.0 g of sulfur reacts with excess oxygen to produce 7.50 g of sulfur dioxide, what is the percentage yield for the reaction?

Answer

Percentage yield = 75.1%

Logic

1 Write a balanced equation.

$S + O_2 \rightarrow SO_2$

2 Calculate the amount of product that can theoretically be produced from the reactants.

$$n = \frac{m}{M}$$

$$n(S) = \frac{5.0}{32.06} = 0.156\,\text{mol}$$

$n(SO_2) = 0.156$

$m = n \times M$

$m(SO_2) = 0.156 \times (32.06 + 2 \times 16)$

$= 9.99\,\text{g}$

This is the theoretical yield or mass.

3 Calculate the percentage yield using the theoretical yield or mass that you have calculated and the actual yield or mass given in the question.

$$\%\ \text{yield} = \frac{\text{actual mass}}{\text{theoretical mass}} \times 100$$

$$= \frac{7.50}{9.99} \times 100$$

$$= 75.1\%$$

Try these yourself

a The synthesis of aspirin (acetylsalicylic acid) involves the reaction:

$C_7H_6O_3 + C_4H_6O_3 \rightarrow C_9H_8O_4 + C_2H_4O_2$

Salicylic acid ethanoic anhydride aspirin/acetylsalicylic acid acetic acid

If 25.0 g of acetylsalicylic acid is produced when 30.0 g of salicylic acid reacts, calculate the percentage yield for the reaction.

b The production of ammonia in the Haber process is typically carried out at approximately 450°C and 200 atm. At this temperature and pressure, 35.0 L of nitrogen gas produces 1.50 kg of ammonia. Calculate the percentage yield for the reaction.

EXPERIMENT 9.1

PERCENTAGE YIELD OF CARBON DIOXIDE

Carbon dioxide is produced during the reaction between calcium carbonate and hydrochloric acid. In an open test tube, this gas will escape the solution and the mass lost will be reflected in the loss of mass of the solution. Using this understanding, we can measure the mass of carbon dioxide produced and thus the percentage yield for the reaction.

Aim

To determine the percentage yield of carbon dioxide in the reaction between calcium carbonate and hydrochloric acid

Materials

- Calcium carbonate chips (approximately 2 g)
- 0.5 mol L^{-1} hydrochloric acid
- Large test tube
- Electronic balance
- 10 mL pipette

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals could splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
0.5 mol L^{-1} HCl is corrosive to skin and clothing.	Wear gloves, safety glasses and an apron.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1. Weigh approximately 2 g of calcium carbonate chips. Record the actual mass.
2. Accurately measure 10 mL of 0.5 mol L^{-1} hydrochloric acid with a pipette.
3. Pour the acid into the large test tube.
4. Accurately measure the mass of the acid and test tube.
5. Add the calcium carbonate chips to the acid and record any observations.
6. When there is no longer any visible reaction, weigh the test tube and its contents.
7. If there is time, repeat the experiment or collate your class's results.

Results

Record your results in a suitable table. If you are doing multiple trials or collating the class results, ensure that you include room for all trials as well as the average.

Analysis of results

1 Write a balanced equation for the reaction.
2 Calculate the number of moles of each reactant used in the reaction.
3 Determine which reactant was the limiting reactant. Did your observations support this?
4 Calculate the mass of carbon dioxide that would theoretically be produced from the reactants.
5 Use your results to calculate the mass of carbon dioxide actually produced in your experiment.
6 Calculate the percentage yield for the reaction.

Discussion

1 What assumption was made in determining the mass of carbon dioxide produced in this reaction?
2 Suggest some reasons why the reaction was not 100 per cent efficient.
3 What were some areas where errors or inaccuracies may have occurred during the experiment?
4 Suggest some ways to improve the method.

Conclusion

What did you conclude regarding the percentage yield in the production of carbon dioxide in this reaction?

INVESTIGATION 9.1

CALCULATING THE PERCENTAGE YIELD

To calculate the percentage yield for a reaction, it is necessary to be able to measure the amount of product produced from a known amount of reactants. In this investigation, you will design and conduct an experiment to determine the percentage yield of the reaction between magnesium and oxygen:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

What is your aim?

What are you trying to achieve with this investigation?

What will you need?

Carefully plan what you will need to conduct the investigation. List the items in detail, making note of the size, quantity, type and concentration where applicable.

What are the risks?

Carefully consider the risks associated with the investigation. Find the MSDS for any chemicals and consider the appropriate actions to minimise any risks. Complete the table below and get your teacher's approval before conducting the investigation.

Complete the risk assessment box before proceeding with your investigation.

What are the risks in doing this investigation?	How can you manage these risks to stay safe?

How will you carry out your investigation?

List the steps that you will take during the investigation. Ensure your steps are clear, concise and detailed.

What results will you collect?

1 Ensure that you are collecting all the necessary data needed to be able to fulfil your aim of calculating the percentage yield.
2 Prepare a table to effectively organise the data that you collect during the investigation.

How will you analyse your results?

List the steps that you will take to use the data that you have collected. Ensure your calculations are clear, correct and that they allow you to calculate the percentage yield.

What have you found?

What is the percentage yield for the reaction between magnesium and oxygen?

Ideas for improvement or further investigation

1 How could you improve your method to obtain more accurate results?

2 What could you do to further investigate the percentage yield for this reaction?

Taking it further

What other reactions could you investigate the percentage yield of? What factors may limit the reactions that you could investigate?

QUESTION SET 9.2

Remembering

1 What is the difference between the rate of the reaction and the yield of the reaction?

2 Where should equilibrium lie to maximise the yield of the reaction?

Understanding

3 What is the maximum yield that is possible for a reaction?

4 Why is it important to remove the product to maximise the yield of a reaction?

5 Explain why the fermentation of glucose using enzymes is a preferred method of ethanol production.

Applying

6 State the two conditions used in the Haber process and justify the use of each.

7 In the synthesis of aluminium chloride, 25.0 g of aluminium hydroxide reacts with hydrochloric acid. If 20.0 g of aluminium chloride is produced, what is the percentage yield for the reaction?

$Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O(l)$

8 Chlorobenzene is used in the production of a range of chemicals, including dyes. Its production can occur through the substitution reaction of benzene with chlorine:

$C_6H_6(l) + Cl_2(g) \rightarrow C_6H_5Cl(s) + HCl(g)$

Calculate the percentage yield for the reaction if 90.0 g of benzene produces 125 g of chlorobenzene.

9 In the synthesis of hydrochloric acid, 3.0 kg of chlorine gas is placed in a chamber with 150 g of hydrogen gas.

- a Write a balanced equation for the reaction.
- b What conditions would favour a high rate of production?
- c Given that this is an exothermic reaction, what conditions would increase the yield of HCl?
- d What is the limiting reactant in this reaction?

9.5 Synthesis of soaps and detergents

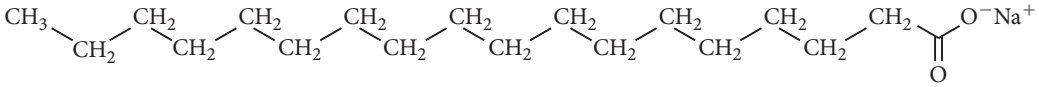
We use **soaps** and **detergents** every day, but how often have you stopped to think about what they are, how they work and how they are made?

Soaps and detergents are generally used as cleaning products because of their ability to remove dirt, oil and stains. This vital property is due to the structure of the soap and detergent molecules. Our knowledge of this structure has enabled us to synthesise more effective cleaning products.

To revise the action of soaps on surface tension, refer to Nelson Chemistry Units 1 & 2, *Chapter 6, page 286.*

Structure of soaps

Soaps are salts of fatty acids. They consist of a long hydrocarbon chain, or tail, with a carboxylate ion (—COO^-) at one end – this is known as the head. A positively charged sodium or potassium ion is bonded to the carboxylate ion, making the soap molecule a sodium (or potassium) salt.



▲ Figure 9.11 The structure of a soap molecule, showing the long hydrocarbon tail and carboxylate ion head

SOAP MODEL

Visit this website to view a model of a soap molecule.

How soaps are made

Soaps are made through the hydrolysis of fats in a saponification reaction. Fats are triglycerides – molecules with three hydrocarbon chains containing 10–20 carbon atoms joined to a propane backbone by three ester bonds. When a triglyceride reacts with sodium (or potassium) hydroxide, the ester bonds break and an alcohol (1,2,3-propanetriol glycerol) and three alkyl carboxylates are formed.

To revise your understanding of esters, refer to Chemistry section 6.9, page 310.

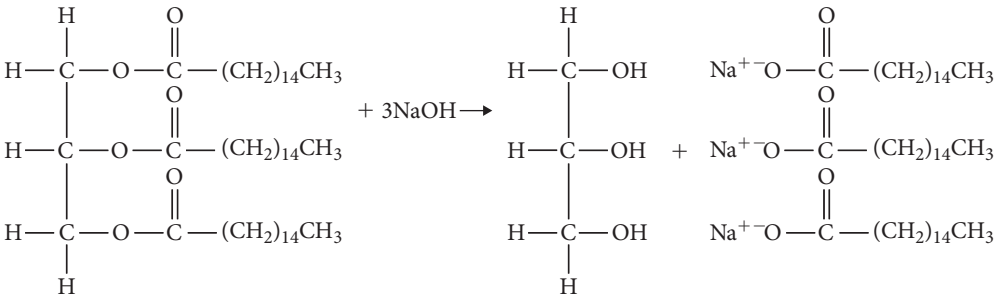


Figure C9.12 ▶
The production of soap

How soaps work

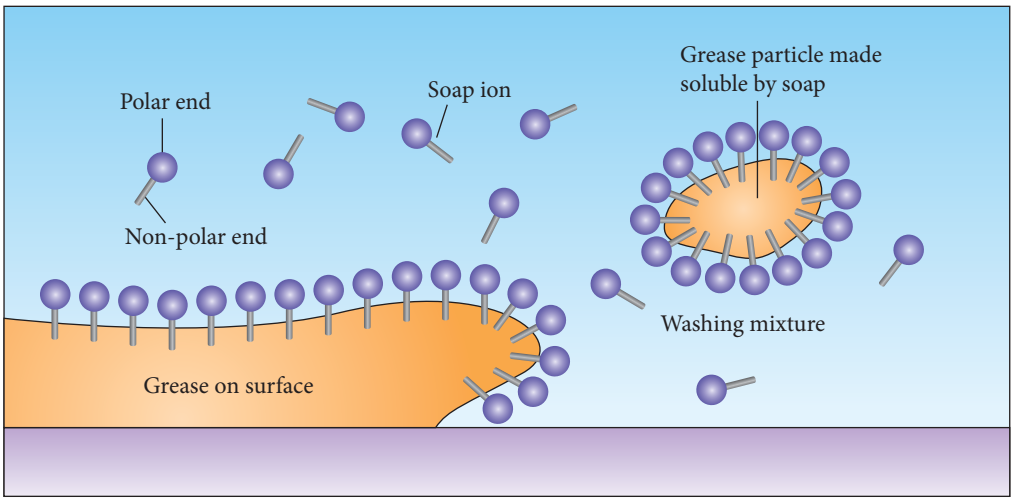
SOAP FORMATION

View this animation to see how soaps are made.

Soaps are able to clean because they can bond with both polar and non-polar substances. The hydrocarbon chain, or tail, is **non-polar**, or **hydrophobic**. This part can bond to non-polar dirt and grease. The head is **polar** due to the presence of the carboxylate ion. It is **hydrophilic** – it can form bonds with water molecules.

Soap molecules surround dirt or grease on a surface, with their hydrophobic tails embedded in the dirt or grease. This leaves the hydrophilic ends on the outside to bond with the water molecules. When the water is agitated, the water molecules pull on the soap molecules, which pull on the dirt. This lifts the dirt away from the surface and more soap molecules are able to surround it. When the soapy water is washed away, the dirt is taken with it.

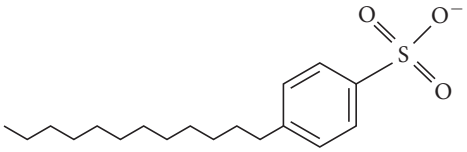
Figure C9.13 ▶
The cleaning action of soap



Detergents

One problem with soaps is that they don't lather up in water containing calcium or magnesium ions – hard water. When the calcium or magnesium ions combine with the carboxylate ions on the soap, they form an insoluble product, resulting in scum. Detergents do not contain the carboxylate ion and therefore do not form the precipitate.

Like soaps, detergents contain a non-polar hydrocarbon chain tail and a polar head. This means that they are able to clean by the same process as soaps. The hydrocarbon tail in detergents is an alkylbenzene while the polar head is a sulfonate (SO_3^-) ion. These are known as anionic detergents due to the negative charge on the ion.



◀ **Figure C9.14**
The structure of an anionic detergent

CLEANSING ACTION OF SOAP

Watch this short animation, which shows how soap works.

9.6 Synthesising fuels

Carbohydrates are fuels that provide an energy source for living things. The oxidation of glucose in cells provides most of the energy needed for life. As well as needing fuels for life we also rely on fuels to produce electricity and power vehicles.

Most fuels are organic compounds. Coal and crude oil, carbohydrates, proteins and fats are all fuel sources used for particular purposes.

As you learnt in *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Context 2, most transport fuels are derived from crude oil. Crude oil is a mixture of many different hydrocarbons and is classed as a fossil fuel because it is formed by the decomposition of prehistoric living things. Since crude oil is a mixture of hydrocarbons, it is processed by fractional distillation.

Fractional distillation cannot produce enough petrol to meet all transport needs, so some of the heavier fractions with a carbon chain with 15–25 carbon atoms are subjected to catalytic cracking. Catalytic cracking is a decomposition reaction in which larger molecules are broken down into two or more smaller molecules (see Chemistry section 7.1).

In 2013, it was estimated that there were 1.3 trillion barrels of proven oil reserve left in the world's major fields, which at present rates of consumption will last 40 years. By 2040, production levels may be down to 15 million barrels per day – around 20 per cent of what we currently consume. It is likely by then that the world's population will be twice as large, and more of it industrialised (and therefore oil dependent).

This means we need new sources of fuels to supplement and eventually replace the current fossil fuels. Two categories of alternative fuels are biofuels, such as ethanol and biodiesel, and hydrogen.

The use of hydrogen as a fuel in fuel cells was discussed in Chemistry section 5.5. In most fuel cells, hydrogen is oxidised at the anode and oxygen is reduced at the cathode. A by-product of the fuel cell is water.

The hydrogen used in fuel cells is produced from water through an oxidation–reduction reaction opposite to the one in fuel cells that consume it.

To revise the production and use of hydrogen as a fuel, refer to Chemistry sections 5.5 and 5.6, pages 264 and 266.

Biofuels

Biofuels are produced from renewable sources such as crops rather than from fossil fuels. Biofuels are classified as renewable sources of fuels because they can be continually produced from crops, algae or animal wastes. The two main biofuels currently used in Australia are ethanol and biodiesel. Ethanol is only used in Australia as a fuel additive, E10, which is a mixture of unleaded fuel and 10 per cent ethanol.

Synthesis of ethanol

There are two main processes used for synthesising ethanol – fermentation and hydration of ethene.

The most common method for the production of ethanol in beverages is fermentation. This process is increasingly being used to produce fuel alcohol and, since 2007, Australia has tripled its production of fuel ethanol through the fermentation process.

For fermentation:

- a suitable grain or fruit is mashed up with water
- an appropriate yeast strain is added
- air is excluded
- the mixture is kept at 37°C.

Enzymes in the mixture convert any starch or sucrose to glucose and fructose, and then the yeast consume the monosaccharides and produce ethanol. The equation for the fermentation of glucose ($C_6H_{12}O_6$) is:

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

The overall reaction involving fermentation is an oxidation–reduction reaction in which carbon is reduced in ethanol and oxidised in carbon dioxide.



Figure C9.15 ▶ Part of Wilmar's bioethanol Sarina distillery in North Queensland, which produces 60 million litres of bioethanol per year by fermenting molasses, a by-product of sugar production

ETHANOL PRODUCTION

Visit this website to find out about how ethanol is made.

USING DILUTE SULFURIC ACID

Watch this video to see how sulfuric acid can be used to hydrate ethene.

The most common method of producing ethanol in the developed world is the hydration of ethylene, which is produced through catalytic cracking as was discussed in section 7.1. Due to the low costs of ethylene as a raw material, approximately 95 per cent of the industrial ethanol made in the developed world is produced in this way. Ethanol produced by this method is not considered a biofuel because it did not come from a crop.

This addition reaction was studied in *Nelson Chemistry Units 1 & 2*, and in section 6.6.

The overall addition reaction can be written:

$$CH_2{=}CH_2(g) + H_2O(g) \rightarrow CH_3CH_2OH(l) \quad \Delta H = -45 \text{ kJ mol}^{-1}$$

Ethylene Ethanol

There are many different processes by which this reaction can occur. One way is to react ethanol with steam, using a catalyst. Another way is to heat ethanol with a dilute sulfuric acid catalyst. Irrespective of which process is used, the same overall reaction occurs.

A high yield for this reaction is favoured by a low temperature. However, at low temperatures, the rate would be too slow. A temperature of approximately 300°C gives a yield of about 5 per cent. A high pressure and catalyst of phosphoric acid increase both the yield and rate of production of ethanol.

Synthesis of biodiesel

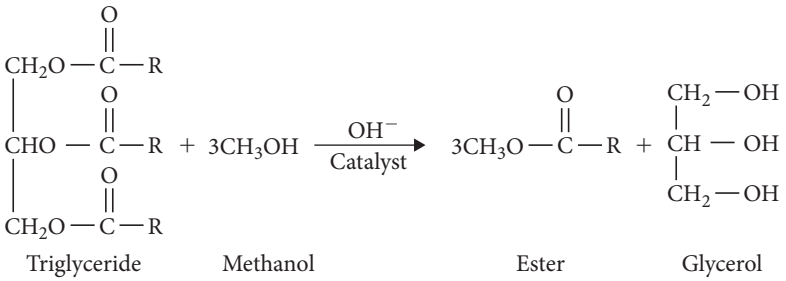
Biodiesel can be produced from almost any fatty acid, including corn, palm, coconut, sunflower and peanut oils. Most biodiesel currently produced uses waste vegetable oil from restaurants,

chip shops and industrial food producers, which means the cost is kept down and the fuel can compete favourably with fossil diesel.

Diesel is a fuel with a long hydrocarbon chain of 8–21 carbons. Biodiesel is similar, but is an ester, containing two oxygens. This is because it comes from plant or animal fats, which are triglycerides.

These react with a short-chain alcohol, usually methanol or ethanol, to produce an ester (the diesel) and glycerol. This process is called **transesterification**.

The reaction with methanol is shown below.



Once the reaction is complete, the two products are gravity separated because the glycerol is denser than the biodiesel. The biodiesel is purified and is then ready for use.

A catalyst is used in the production of biodiesel to facilitate a rapid reaction rate. Three main catalysts are used:

- base catalysts
- acid catalysts
- enzymes.

Almost all biodiesel production uses a strong base, often sodium or potassium hydroxide. This method is effective because it is the most economical, has a 98 per cent conversion yield and requires low temperatures. However, it produces high temperatures, which are safety risks, and forms soap, which reduces the yield of the ester. Also it is expensive to purify the glycerol due to the presence of the base.

Alternatively, an enzyme, or biological catalyst, can be used. Lipase catalyses the break down of fats and thus it can be used to increase the rate of the reaction. This method overcomes the problem of soap production and therefore enables a higher yield of biodiesel. However, the enzymes are expensive to produce.

Another factor to consider is the yield of biodiesel. This is maximised by ensuring that the alcohol is in excess, which favours the forward reaction and therefore the production of diesel.

Ethanol can be synthesised by oxidation–reduction and addition reactions and biodiesel can be synthesised by esterification reactions.

HOW IT'S MADE – BIODIESEL PRODUCTION

Watch this video about the processes involved in the production of biodiesel.

BIODIESEL PRODUCTION IN AUSTRALIA

Visit this website to find out where biodiesel is produced in Australia.

QUESTION SET 9.3

Remembering

1 What is a biofuel?
2 Why are biofuels produced?
3 What other important fuel is produced and used that is not a biofuel?

Understanding

4 a Name the two types of chemical reactions through which ethanol is produced.
  b Should the ethanol produced through both these reactions be considered a biofuel? Why or why not?
5 Write the half reactions for the fermentation of glucose to ethanol and water. Label each half reaction as oxidation or reduction.
6 Draw a diagram showing the production of biodiesel using ethanol instead of methanol.

Analysing

7 Is biodiesel a better fuel than fossil diesel? Explain why or why not.

9.7 Green chemistry

Green chemistry is a relatively new area of chemistry that aims to reduce the impact of chemistry on the environment by reducing or eliminating the use or production of hazardous substances. As we learn more about the impact of chemicals on the environment, the importance of green chemistry becomes more evident.

Green chemistry requires that all aspects of chemical production be analysed to ensure that nothing potentially harmful is used or produced. This adopts the philosophy of 'prevention is better than cure'. Previously, additional steps were used to deal with the hazardous chemicals after their production. Green chemistry means that they are not produced in the first place.

The idea of green chemistry originated with the US Federal Pollution Prevention Act in 1990. This act included a hierarchy associated with pollution:

1 Prevent pollution.
2 Treat chemicals to make them safe prior to disposal.
3 Dispose of untreated chemicals safely.

If it is not possible to achieve the first point in the hierarchy, then you move to the next point. If this is not possible, then the third point is followed. More specifically, when designing a process, the aim is to ensure there is no pollution. If hazardous products are produced, then they should be treated before they are disposed of. If it is not possible to treat the chemicals, then they should be disposed of in a safe manner.

By following this hierarchy when designing reactions, scientists are able to implement green chemistry as they will be reducing or eliminating the hazardous chemicals that humans and the environment are exposed to.

US Environmental Protection Agency



▲ Figure C9.16
The United States Environmental Protection Agency's logo for green chemistry

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Visit this website to learn more about green chemistry.

Green chemistry reduces the impact of chemistry on the environment by reducing or eliminating hazardous chemicals.

ACTIVITY 9.1

BUILDING A BETTER BLEACH

Aim

To gain a better understanding of green chemistry by considering the production of bleaching agents

You will need

- Access to the internet

What to do

1. Use the weblink to access and read the article about chemicals used to treat stains on our clothes.
2. In small groups, discuss how the change to hydrogen peroxide to treat stains is an example of green chemistry.

What did you discover?

Write a paragraph summarising your discussion.

BUILDING A BETTER BLEACH

Visit this website and read the article on green chemistry and bleach.

Designing green reactions

When scientists are designing synthesis reactions, they should adhere to the 12 principles of green chemistry. These principles address the different stages of reactions and the areas where hazardous substances may be used or generated.

The 12 principles of green chemistry

1. *Prevent waste:* By not producing waste there is no waste to clean up at the end of the process.
2. *Maximise atom economy:* Atom economy refers to the amount of reagent atoms that are present in the desired product. By maximising the number of atoms used that are in the desired product, there are fewer atoms left over at the end of the process. This reduces waste.
3. *Design less hazardous chemical syntheses:* Design the synthesis process to use and generate chemicals that are not hazardous to humans or the environment.
4. *Design safer chemicals and products:* If the chemicals that are being designed are hazardous, then the process is going against the principles of green chemistry. Rather, design and produce chemicals that are equally effective but less hazardous.
5. *Use safer solvents and reaction conditions:* When additional chemicals are required for the process, use safe ones.
6. *Increase energy efficiency:* High temperatures and pressures require energy. Therefore, use room temperature and pressure where possible.
7. *Use renewable reactants:* Consider the types of reactants used. **Renewable reactants** can be replenished. Using waste products of other processes will also be greener chemistry.
8. *Avoid using chemical derivatives:* Chemical derivatives have had to go through previous processes, thus using more reactants and reactions.
9. *Use catalysts:* Catalysts are effective in small quantities and can be reused. This means less use of chemicals.
10. *Design chemicals that will degrade:* Degradable products will mean fewer chemicals in the environment.
11. *Prevent pollution:* Monitor the reaction in real time to control the reaction and avoid by-products.
12. *Minimise the potential of chemical accidents:* Choose chemicals, including their phases, that minimise the chance of accidents including explosions, fires and chemical release to the environment occurring.

PRINCIPLES OF GREEN CHEMISTRY BOOKMARK

Visit this website to download a bookmark with the 12 principles of green chemistry.

To see how the wine industry is applying these principles, refer to Context 1, 'Wine', page 25.

Green chemistry principles include using renewable materials, using safe solvents and reducing unwanted products.

To see an application of green chemistry, refer to Context 4, 'Polymer chemistry', page 102.

WOW

The greening of ibuprofen

Ibuprofen is an analgesic commonly used in pain relief. It was originally synthesised by The Boots Company in a six-step method with an atom economy of only 40.0 per cent. This meant that there was a large amount of wastage in the process.

In the mid-1980s, a number of companies combined to form the BHC Company with the aim of producing a greener synthesis of ibuprofen. This resulted in a three-step method with much less wastage and an atom economy of 77 per cent.

The significance of this development was recognised by The BHC Company receiving both the coveted Kirkpatrick Chemical Engineering Achievement Award in 1993 and the Presidential Green Chemistry Challenge Award in 1997.

Atom economy

Atom economy refers to the mass of reactants that contribute to the desired product. The greater the atom economy, the less wastage of atoms and the greener the chemistry.

$$\text{Atom economy} = \frac{\text{mass of atoms in the desired product}}{\text{mass of atoms in the reactants}} \times 100$$

The importance of atom economy was recognised in 1998 when Professor Barry Trost was awarded the Presidential Green Chemistry Challenge award. His work developed the ideas of reducing the use of non-renewable sources, reducing the amount of waste and decreasing the number of steps used to synthesise the desired product. These considerations combine to increase the proportion of reactant atoms that end up in the desired product, thereby increasing the atom economy and decreasing the waste atoms.

WORKED EXAMPLE 9.3

Calculate the atom economy in the following reaction used to synthesise calcium oxide:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Answer

Atom economy = 56.0%

Logic

1 Calculate the molar mass of the reactants.

$M(CaCO_3) = 40.1 + 12.01 + 3 \times 16$

$= 100.11$

2 Calculate the molar mass of the desired product.

$M(CaO) = 40.1 + 16$

$= 56.1$

3 Calculate the atom economy. (Note: Multiply the molar mass of each reactant or product by its coefficient.)

$$\text{Atom economy} = \frac{\text{mass of atoms in the desired product}}{\text{mass of atoms in the reactants}} \times 100$$

$$= \frac{56.1}{100.11} \times 100$$

$$= 56.0\%$$

Try these yourself

a Calculate the atom economy for the synthesis of ammonia in the Haber process:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

b What is the atom economy in the following reaction used to produce ethene?

$C_{10}H_{22} \rightarrow C_2H_4 + C_8H_{18}$

ACTIVITY 9.2

MODELLING ATOM ECONOMY

Aim

To use the combustion of methane to model atom economy in the production of carbon dioxide

You will need

- Molecular model kit
- Calculator

What to do

1. Write the balanced equation for the combustion of methane.
2. Use the molecular model kit to make molecular models of the reactants.
3. Calculate the molecular mass of the total reactants.
4. Use your models of methane and oxygen to 'react' and form carbon dioxide and water in the appropriate proportions as shown in your equation.
5. Calculate the molecular mass of the carbon dioxide produced.
6. Observe the atoms in the water – these atoms are waste as they are not part of the desired product.
7. Calculate the atom economy for the reaction.

What did you discover?

1. Would you consider this reaction to be an example of green chemistry?
2. Your calculations assumed that there was a 100 per cent yield in the reaction. What would happen to the atom economy if the yield was lower?

QUESTION SET 9.4

Remembering

1. Define 'green chemistry'.
2. List the steps in the hierarchy to be followed in green chemistry.
3. Draw the general structure of a soap molecule.
4. Why are detergents better to use than soaps in hard water?

Understanding

5. Choose one of the 12 principles of green chemistry. Explain how implementing this principle makes a chemical process more environmentally friendly.
6. Explain how soaps are able to remove grease and dirt from surfaces.

Applying

7 Calculate the atom economy for one of the reactions involved in the extraction of iron:

$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(l) + 3CO_2(g)$

8 Write an equation for the synthesis of a soap molecule of $CH_3(CH_2)_{16}COO^-Na^+$.

Reflecting

9 Discuss the importance of green chemistry and the implications if green chemistry is not used during synthesis reactions.

CHAPTER CHECKLIST

You should know:

- synthesis reactions involve using chemical reactions to produce a specific product
- synthesis reactions can produce a wide range of products
- synthesis reactions are designed to produce the product in the most economical, safe manner
- a common method of identifying an appropriate reaction pathway and initial reactants is to use retrosynthetic analysis where you start with the desired product and work backwards by removing simple sections
- the chosen reaction mechanism or pathway should be safe, efficient and cost-effective
- most reaction pathways are multistep. Often, the product from one reaction is used as a reactant for the next. These chemicals are called intermediates
- multistep reaction pathways may be linear or convergent
- the limiting reactant is the reactant that gets used up first. It can be calculated by comparing the actual ratio with the stoichiometric ratio
- the yield of a reaction is the percentage of possible product that is actually produced
- the percentage yield is calculated by dividing the actual yield by the theoretical yield and multiplying by 100
- the yield of the reaction is maximised by choosing conditions that favour the forward reaction and therefore shift equilibrium to the right
- the contact process synthesises sulfuric acid
- the Haber process synthesises ammonia
- green chemistry is the area of chemistry that aims to reduce the impact chemistry has on the environment
- how to relate types of reaction to the formation of fuels
- atom economy is the percentage (by mass) of the reactants that form the desired product. Green chemistry aims to increase the atom economy to reduce the wastage in reaction pathways.

You should be able to:

- explain processes for making biofuels and hydrogen.

CHAPTER GLOSSARY

atom economy the percentage (by mass) of the reactants that form the desired product

biofuel an energy source produced from renewable sources such as crops

combustion reacting with oxygen

contact process a series of reactions to produce sulfuric acid

convergent sequence a sequence in which the reaction steps run parallel before the reactants of two separate pathways are combined

detergent alkylbenzene sulfonate salt; hydrophobic hydrocarbon end (alkylbenzene) with a hydrophilic sulfonate ion end

endothermic reaction a reaction that absorbs energy from the surroundings; the products have more energy than the reactants

enzyme a protein that catalyses chemical reactions in living organisms by orienting molecules in the correct manner and lowering the activation energy

equilibrium the state for a reversible reaction in a closed system when the forward and reverse reactions occur at the same rate

excess reactants or reagents the reactant that is left over when the limiting reactant is used up

exothermic reaction a reaction that releases heat energy to the surroundings due to the products having less energy than the reactants

green chemistry the area of chemistry that aims to reduce the impact of chemistry on the environment

Haber process the industrial process that combines nitrogen and hydrogen gases to produce ammonia on a large scale

heat of reaction the amount of energy absorbed or released in a reaction

hydrophilic attracting water; 'water loving' and capable of forming bonds with water

hydrophobic more attracted to particles of the same type than to water, usually immiscible with water; 'water-hating' and cannot bond with or dissolve in water

intermediate a product of one reaction that is used as a reactant in the next reaction of a reaction pathway

limiting reactant or reagent the reactant that is used up first and therefore limits the amount of product produced

linear sequence a sequence in which the reaction steps follow one after the other in a linear progression.

non-polar having no charged ends or poles

percentage yield the percentage of the possible product that is actually produced

polar having charged ends or poles

reaction mechanism the sequence of chemical reactions for an overall chemical change (reaction pathway)

reaction pathway the sequence of chemical reactions for an overall chemical change (reaction mechanism)

renewable reactant a reactant that is renewable

retrosynthetic analysis a process for determining the reaction pathway for a synthesis reaction that involves starting with the product and working backwards by identifying simpler substances

soap a salt of a fatty acid; hydrophobic hydrocarbon chain with a hydrophilic carboxylate ion end

synthesise to make something; with respect to chemistry, to produce a specific product

transesterification the process of reacting a triglyceride with an alcohol to form an ester and glycerol

yield the amount or percentage of the possible product that is actually produced

CHAPTER REVIEW QUESTIONS

Remembering

1. State the aim of synthesis reactions.
2. Define 'atom economy' and state the method for calculating the atom economy of a reaction.
3. Define 'reaction mechanism'.

Understanding

4. Explain how using a catalyst can help make a reaction fit with the aims of green chemistry.
5. Explain why equilibrium is important in synthesis reactions.
6. How is atom economy different to percentage yield?
7. Why is a convergent sequence often preferred over a linear sequence?
8. Name two biofuels and the type of reactions by which they are synthesised.

Applying

9. Ozone breaks down to form oxygen gas in a two-step reaction:
   $O_3(g) \rightarrow O_2(g) + O(g)$
   $O_3(g) + O(g) \rightarrow 2O_2(g)$
   Identify the reactant, intermediate and product.

10 The following reaction is an exothermic reaction:

$CaO(s) + H_2O(l) \rightleftharpoons Ca(OH)_2(s)$

Describe the effect on the yield of the reaction if the temperature is decreased.

11 During the production of oxygen gas by the electrolysis of water 100mL reacts producing 65.0g of oxygen gas.

$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$

a Calculate the atom economy for the reaction.

b Calculate the percentage yield of the reaction.

Analysing

12 Why is ethanol produced by fermentation considered to be a biofuel yet ethanol produced by hydration of ethene is not when they are the same product?

Reflecting

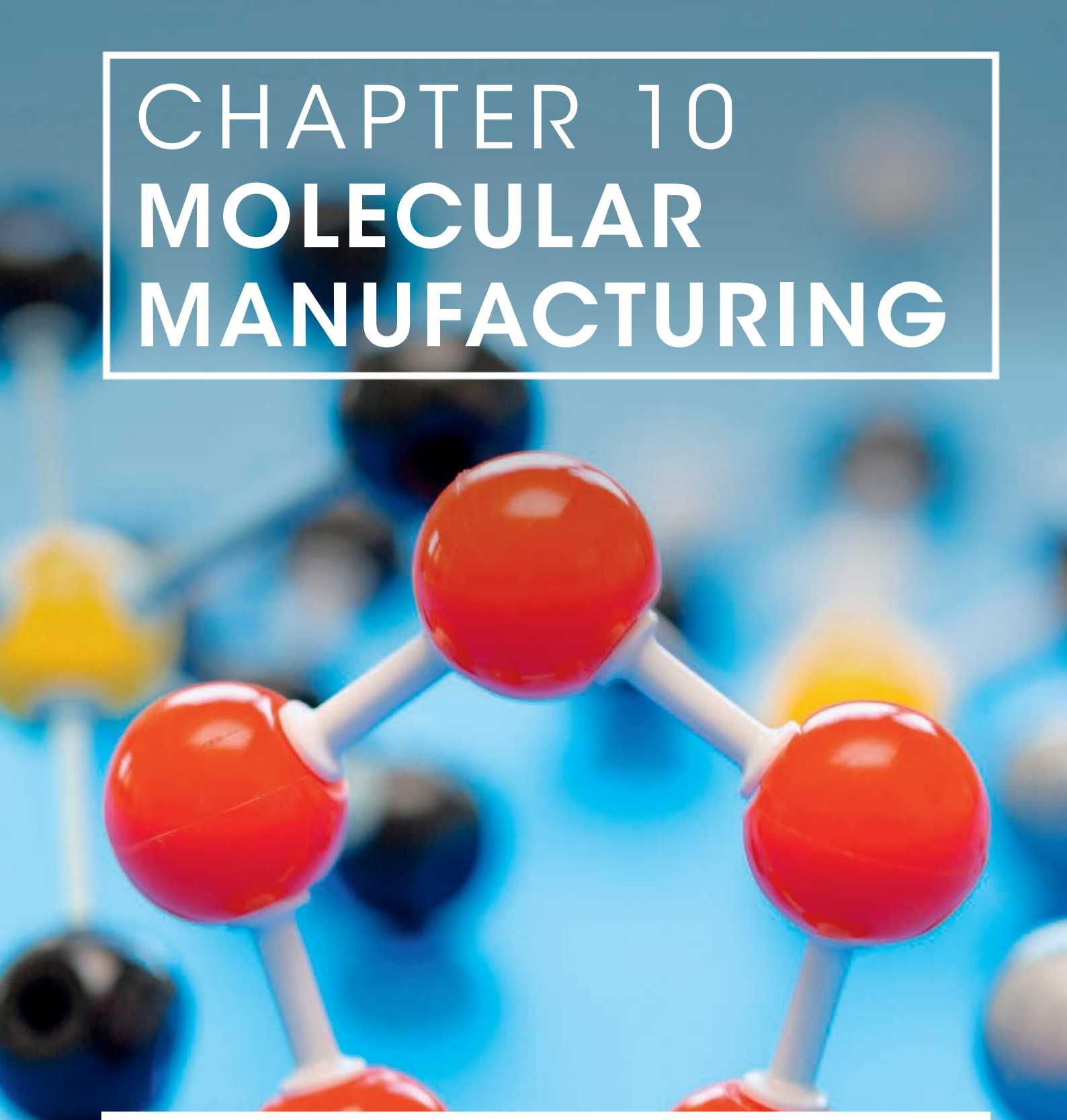
13 How might life be different if we could not manufacture penicillin by synthesis reactions?

14 Discuss some possible reasons why green chemistry was not implemented when synthesis reactions were first developed.

15 What arguments would you put forward to the chief executives of drug companies to encourage them to implement green chemistry?

16 Why is ethanol produced by fermentation considered to be a biofuel yet ethanol produced by hydration of ethylene is not, when they are the same product?

CHAPTER 10
MOLECULAR MANUFACTURING



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By the end of this chapter you will have covered the following material.

Science Understanding

- Molecular manufacturing processes, including protein synthesis, involve the positioning of molecules to facilitate a specific chemical reaction; such methods have the potential to synthesise specialised products (for example: carbon nanotubes, nanorobots, chemical sensors used in medicine) (ACSCH138)

10.1 What is molecular manufacturing?

Molecular manufacturing is the production of molecules, crystals and other chemical structures that have been designed to have a specific shape or chemical composition. The products have specific properties that are related to this shape or chemical make-up. These materials are incorporated into fabrics, batteries, medical devices and many other products. Devices and applications that incorporate these manufactured molecules have many advantages over more conventional versions. For example, batteries have been manufactured that have hundreds of times the battery life of current battery technology. Molecular manufacturing has also allowed the development of innovative technology such as specialised drug delivery systems that can target disease in the body. This has made treatment more effective and patients suffer fewer side effects.

Macro vs nano properties

Most molecular manufacturing involves manipulation of structures at the nano level. This makes **nanotechnology** very important in molecular manufacturing.

Nanotechnology is science, engineering and technology that occur at the nanoscale, around 1–100 nanometres. A **nanometre** (nm) is extremely small, just one-billionth of a metre. Figure C10.1 shows how some common objects compare in size. When we look at things on the nano scale, we are talking about objects the size of atoms and molecules.

The following measurements demonstrate how small a nanometre is:

- A gold atom is 0.3 nm in diameter.
- A human hair is 100 000 nm thick.
- A strand of human DNA is 2 nm in diameter.

Nanoparticles behave very differently from the same particles on the macro scale. When particles are between 1 and 100 nm, their properties change compared to the same substance on the macro scale. For example, as a particle becomes smaller, the surface area of the substance becomes much larger and this affects the way it reflects light. This can result in a substance such as gold, which is yellow when the particles are macro sized, being either red or purple when the particles are nano sized.

SIZE AND SCALE

Use this interactive tool to investigate the size of objects.

WOW

Ancient and medieval nanotechnology

Nanotechnology has been used unwittingly throughout history. The medieval makers of stained glass windows trapped silver and gold nanoparticles in the glass matrix, which reflected light differently depending on their size. The gold nanoparticles could be red, green or orange depending on their size (50–100 nm). The silver particles could be blue, dark orange or yellow (40–100 nm).

In Italy around 1450–1600, artists created ceramic plates and bowls using copper and silver particles between 5 and 100 nm. Depending on how the light reflects off the different particles, the colour changes, making the object iridescent. Even earlier than this, the Chinese used gold nanoparticles as a dye in their porcelain.

The Lycurgus Cup is a Roman cup created around the fourth century. It is made from glass that contains gold and silver nanoparticles. In daylight it appears green. But if light is shone directly through the glass, it appears red.



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▲ **Figure C10.2** A medieval stained glass window contains nanoparticles that reflect light and create colour.



A 6-foot tall man is 1.83 metres or nearly 2 billion nanometres tall.



Pin: 1 mm wide

10^{-2} m — 1 cm, 10 mm

10^{-3} m — 1000000 nm = 1 mm

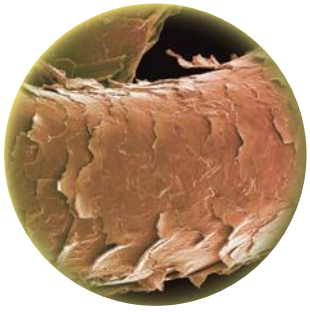


Ant: 5 mm wide



Dust mite: 200 μm wide

10^{-4} m — 0.1 mm, 100 μm



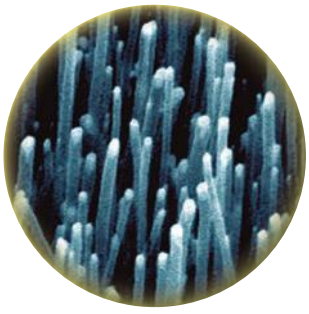
Human hair: 10–150 μm wide

10^{-5} m — 0.01 mm, 10 μm



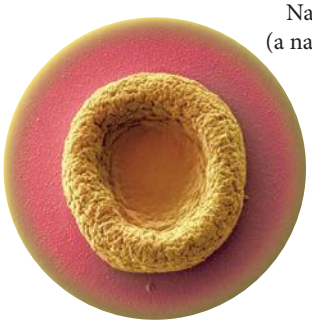
Nano bull: 10 μm wide (a nano sculpture produced by lasers)

10^{-6} m — 1000 nm = 1 micrometre (μm)



Nanowires: 70 nm wide

10^{-7} m — 0.1 μm, 100 nm



Blood cell: 2.5 μm wide

10^{-8} m — 0.01 μm, 10 nm



Nanotubes: 1 nm wide

10^{-9} m — 1 nanometre = 1nm



DNA: 2 nm wide

10^{-10} m — 0.1 nm

▲ **Figure C10.1** Sizes of some objects

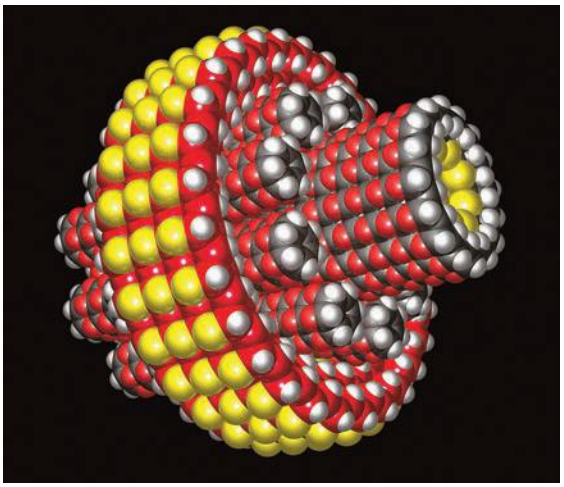


Figure C10.3 ▶ An artist's impression of a nanomachine. This is a molecule created to perform a very specific task such as building a larger molecule like a protein.

Other properties that change between the macro and the nano scale are melting point, conductivity, magnetic properties, chemical reactivity and fluorescence, which is the ability of a substance to emit light when it has absorbed energy.

How is molecular manufacturing done?

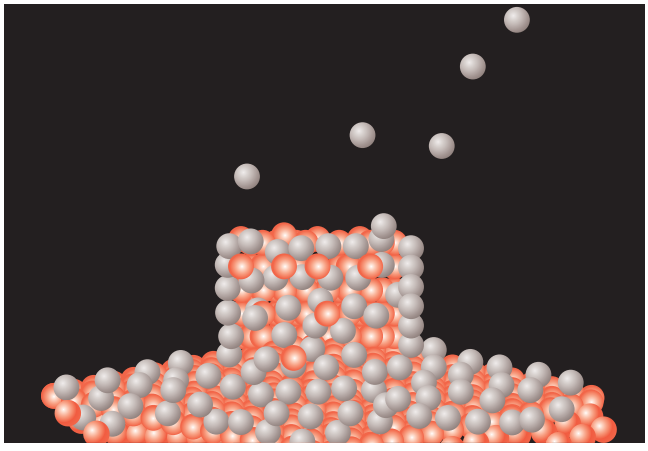
Molecular manufacturing can be performed in many ways. We will consider three broad methods.

The first method is the **orientation effect**, also sometimes referred to as **mechanosynthesis**. This involves positioning molecules so that the desired **functional groups** line up, all reactions are efficient and there is less waste and fewer undesired products forming. This occurs naturally in processes such as **protein synthesis** and **DNA replication**.

Specifically manufactured proteins can be built in the form of a molecular machine called a **nanomachine**. Nanomachines can manufacture molecules as suggested in Figure C10.3.

The second method is the manipulation of structures on the atomic and molecular level. This is done in two ways. You can alter, manipulate or control the bonding between atoms, ions and molecules. If the bonds that form can be controlled, then specific properties can be given to the final structure. Or you can build substances by adding or substituting specific atoms in a structure. This can be seen in Figure C10.4. This also gives the final structure very specific properties. In this manner, chemicals and materials can be tailored for a specific purpose, as can be seen in Figure C10.5.

To see applications of molecular manufacturing, refer to Context 6, 'Molecular manufacturing', page 125.



▲ **Figure C10.4** Atoms being added individually to a structure to create a very specific final molecule



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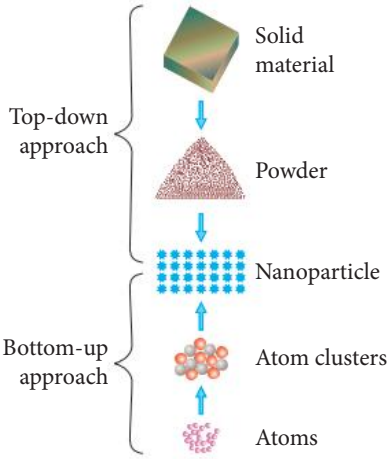
▲ **Figure C10.5** This material is a nanofabric that does not absorb water or other liquids. The properties of the fabric have been changed so that the water beads rather than being absorbed.

The third method is the use of **protecting groups**. Large molecules often have many reactive sites and/or functional groups. Sometimes a different functional group will react rather than the one you have targeted and a non-desired product is formed. This is wasteful and leads to a reduced **yield** of the desired product. These functional groups can be prevented from reacting by adding a protecting group.

Top-down and bottom-up approaches

A **top-down approach** to molecular manufacturing involves starting with a larger substance and converting it into a smaller, more useful substance, or only keeping part of the original substance. This can be done by removing atoms, grinding or crushing the substance or breaking it into smaller parts. This approach often requires vast amounts of energy and materials and results in a lot of waste.

A **bottom-up approach** involves building a desired structure from the atomic and molecular scale, by adding atoms individually or by adding molecules together to make a larger, more complex molecule. This method is much harder because you are working on the atomic scale, but has less waste and requires much less energy.



◀ **Figure C10.6**
Comparison of the top-down and bottom-up approach to making the same nanoparticle

QUESTION SET 10.1

Remembering

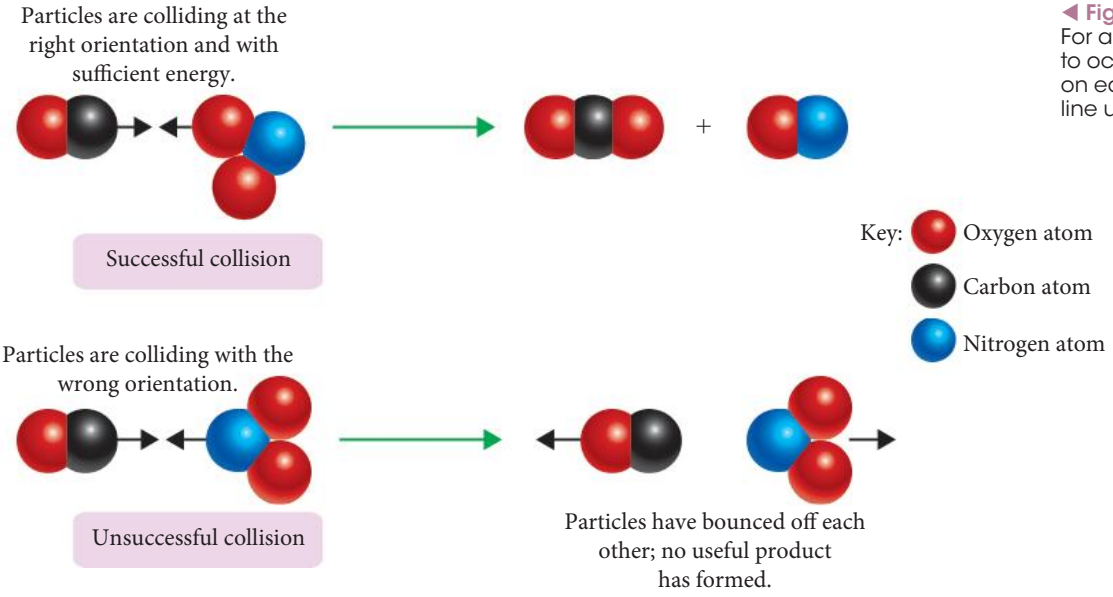
1 What is molecular manufacturing?
2 What is nanotechnology?
3 Describe the difference between a top-down and a bottom-up approach to molecular manufacturing.

Understanding

4 Explain why nanoparticles are useful, using an example in your answer.
5 Using your knowledge of organic chemistry, explain why protecting specific functional groups might be useful in the formation of a specific product.

10.2 Orientation effect

Collision theory says that when molecules move around, they come into contact at random with other molecules. If the right molecules come together with sufficient energy and in the right way, they will undergo a reaction and form a product. In larger molecules, only certain sites on the molecule will take part in a reaction. If two molecules are to react, then the correct sites on both molecules must make contact for a reaction to occur. This can be seen in Figure C10.7.



◀ **Figure C10.7**
For a successful reaction to occur, the correct sites on each molecule must line up.

In mechanosynthesis, reactive molecules are attached to molecular mechanical systems. The different molecules are brought together in a specific position so that the functional groups and reactive sites that need to react are in the correct orientation.

You can picture this like a factory that is putting together a car. The bare skeleton of the car needs to be lined up perfectly with the door, roof and other panels for them to be attached to the car properly. The roof panel needs to come down from above, the door panels from the side and the bonnet needs to be at the front of the car skeleton. If the roof were to come in from the side, then the car would not be put together properly.

These molecular mechanical systems can also keep reactive functional groups apart so they do not react, simply by orienting these groups away from each other.

In nature, there are already mechanisms inside organisms that perform this type of mechanosynthesis. A **ribosome** is a large molecular machine that allows the production of proteins inside cells. The aim of chemists is to synthesise molecular machines similar to ribosomes that can make specifically designed structures.

Protein synthesis

Proteins are found in all living organisms. Proteins can be structural, such as keratin, which is found in skin, fingernails, horns and hair. Another structural protein is collagen, which is found in tendons, animal hides and cartilage. Other proteins have specific jobs to do inside the body. **Enzymes** are proteins that perform many tasks such as getting rid of waste, breaking down molecules such as starch or fats, synthesising DNA or taking part in metabolic pathways including **respiration** or **photosynthesis**. Other examples of proteins are:

- insulin, a hormone that helps to control glucose metabolism in the body
- haemoglobin, which carries oxygen to the cells
- **antibodies**, which help fight disease.

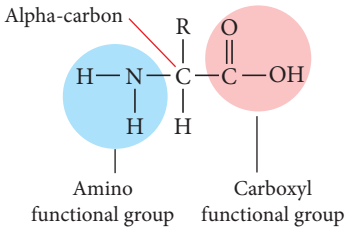


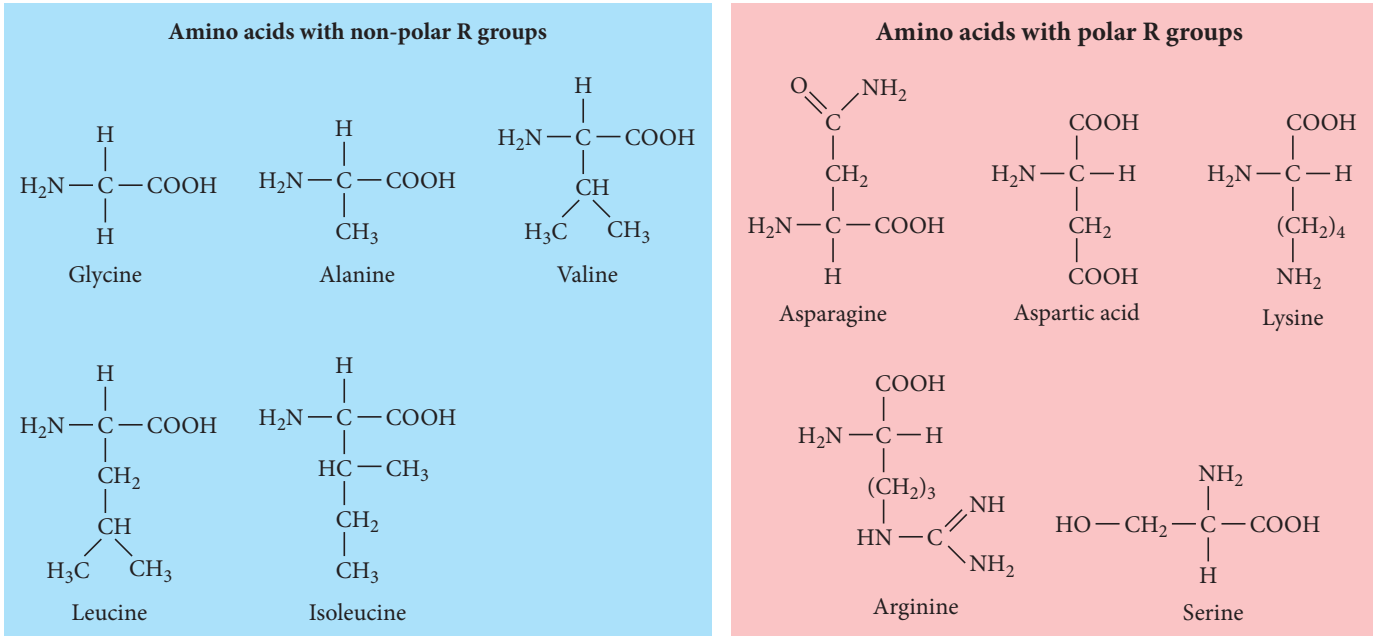
Figure C10.8 ▲ The structure of an amino acid

Amino acids

The basic unit of a protein is the **amino acid**. An amino acid is a molecule with a defined structure seen in Figure C10.8. All amino acids have an amine group at one end and a carboxylic acid at the other. There is a central carbon atom with a hydrogen on one side and an R group on the other.

The R group is what makes each amino acid different. There are 20 natural amino acids that occur in proteins with 20 different R groups. Some of these 20 amino acids are seen in Figure C10.9. Some amino acids have R groups containing polar functional groups such as the hydroxyl group. Others have non-polar R groups with hydrocarbon chains or benzene within their R group. Some have acidic or basic R groups, and two of these 20 amino acids have sulfur-containing R groups.

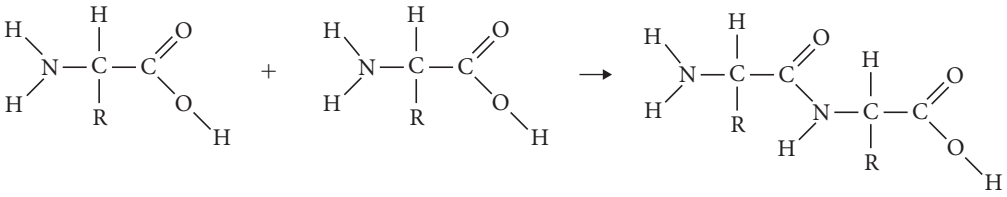
Several amino acids have functional groups that can form ions. For example, the amine group can become **protonated** in the presence of an acid to form a positively charged ion. The carboxylic acid group can donate one of its protons to form the negatively charged carboxylate ion.



▲ Figure C10.9
Some common amino acids

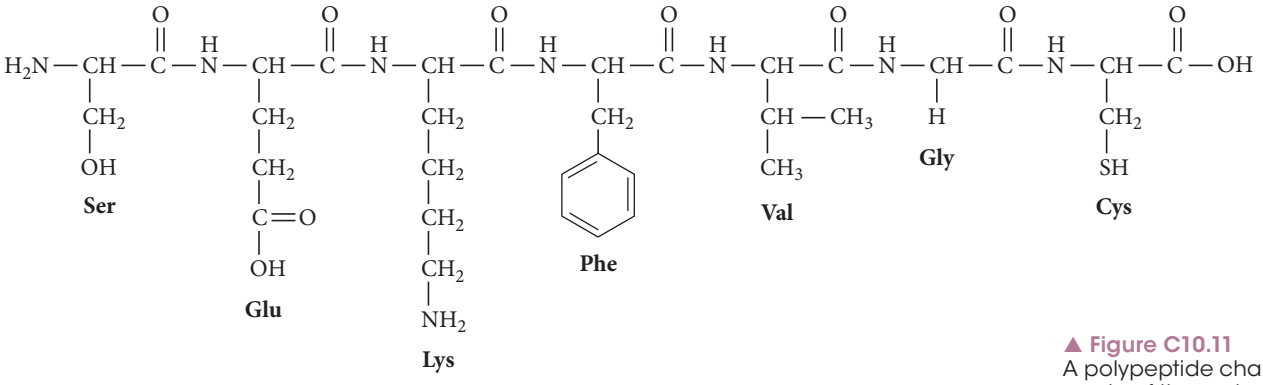
Joining amino acids

To form the primary structure of a protein, a strictly defined sequence of amino acids is joined to make a long chain of amino acids called a **polypeptide**. The amino acids are often referred to as peptide units, so a long chain of them is called a polypeptide. When amino acids join, the amine group from one amino acid joins with the carboxylic acid of another. The resulting structure is called a **dipeptide**.



◀ Figure C10.10
Joining amino acids to make a dipeptide

To form a polypeptide, many amino acid units join together in a specific sequence. A polypeptide chain can be seen in Figure C10.11. Each different protein has a unique sequence of amino acids. All molecules of the same protein have the same sequence.



▲ Figure C10.11
A polypeptide chain made of the amino acids serine, glutamine, lysine, phenylalanine, valine, glycine and cysteine. Each amino acid is represented by its first three letters.

For a dipeptide or a protein to form, the two functional groups must line up perfectly. If two amine groups come into contact, then they will not join. Many of the amino acids are quite large and it is unlikely that the correct functional groups would come into contact if they were just randomly floating around.

ACTIVITY 10.1

MODELLING DIPEPTIDES

Aim

To create molecular models of amino acids and the dipeptides formed from them

You will need

- Molecular modelling kit with carbon, hydrogen, nitrogen, sulfur and oxygen atoms. If you don't have a molecular modelling kit, then you can use plasticine of different colours and toothpicks as bonds.

What to do

1. Using Figure C10.9, create some simple amino acid models, such as glycine, alanine, valine, aspartic acid, lysine, serine and leucine.
2. Join two amino acids to make an amide bond. This structure is called a dipeptide. Draw the molecule you have made, circling the amide link that has formed between the two amino acids.
3. Repeat steps 1 and 2 for at least three different pairs of amino acids.
4. Join glycine with aspartic acid. Compare your dipeptide with other groups' models.
5. Join a number of amino acids into a longer chain made from at least four amino acids. Draw your structure, identifying the amide links.

What did you discover?

1. This reaction is a condensation reaction. Based on what you found when you joined the amino acids, explain why it is called a condensation reaction.
2. Explain what happened when you joined glycine and aspartic acid. Did you all get the same molecules? If not, explain why this occurred.

How do amino acids line up so perfectly?

The blueprint for every protein in a living organism is found in the DNA in its cells. Figure C10.12 shows the major steps of how protein synthesis occurs in a cell.

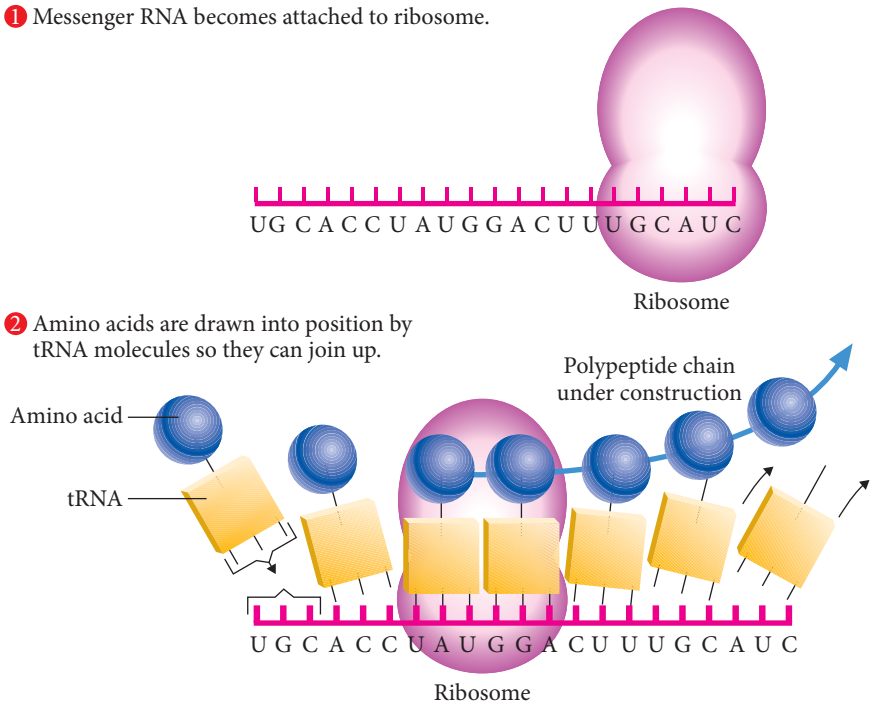


Figure C10.12 ▶ Protein synthesis using a ribosome

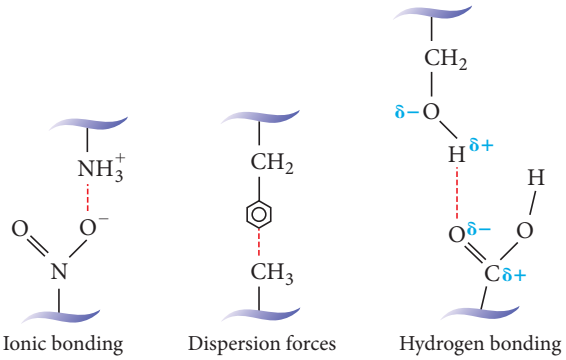
A molecule called **messenger RNA** (mRNA) makes a copy of the DNA code in the nucleus needed to synthesise the protein. The mRNA leaves the nucleus and a large ribosome surrounds the mRNA. The ribosome links the amino acids together in the correct sequence as specified by the mRNA. A ribosome has two sections, called subunits. The small subunit reads the mRNA; the larger unit joins the amino acids together to make a polypeptide chain.

The amino acids are carried on the molecule **transfer RNA** (tRNA), which collects a specific amino acid, then lines up with the matching part of the mRNA.

The ribosome acts like the car factory described earlier. Its job is to ensure that each amino acid is in the correct place so that the carboxylic acid and amine functional groups are lined up to create the long polypeptide chain. A ribosome is a naturally occurring molecular machine that makes polypeptide chains.

Folding of a protein

Once the polypeptide chain has formed, the protein could fold into one of two secondary structures as seen in Figure C10.12. This folding occurs due to hydrogen bonds forming between the peptide or amide links. One structure that can form is called an **alpha helix**. The polypeptide chain forms a structure like a spiral staircase by folding back on itself. The peptide links then form hydrogen bonds to keep the structure in this spiral, folded shape. Another structure is called a **beta-pleated sheet**. When two different polypeptide chains run in opposite directions, they can join through hydrogen bonds that form between the peptide groups on different polypeptide chains. See Figure C7.29 on page 359 for protein formation.



◀ **Figure C10.13**
Different types of bonds forming between R groups make the tertiary structure of a protein.



To revise protein formation and structure, refer to Chemistry section 7.6, page 354.

The primary and secondary structures undergo further interactions, seen in Figure C10.13, to fold into the tertiary structures. These form when the R groups form bonds between themselves. As the R groups on amino acids can be polar or non-polar, ionic or molecular, many different types of bonds form. Hydrogen bonds, ionic bonds and even covalent bonds can form, depending on the R group.

Ionic groups, such as a protonated amine or a carboxylate ion, form strong ionic bonds (referred to as salt bridges) between the chains. When non-polar groups such as benzene molecules or carbon chains are next to one another, then weak dispersion forces will form between the chains. Polar groups such as alcohol or carboxylic acid groups can form hydrogen bonds between the chains.

The final structure, the quaternary structure, forms when several tertiary structures bond together. This does not form in all proteins.

CHIRALITY

Use this interactive tool to arrange the two molecules in the same position.

Artificial protein synthesis

Scientists have the ability to grow proteins in bacterial cells. Genetically modified bacteria have been used to produce diabetes medications, clotting drugs to treat haemophilia and human growth hormone to treat dwarfism. But bacteria cannot produce all the proteins we need.

Artificial peptides and proteins can also be synthesised in the laboratory. The most common method used is solid phase peptide synthesis (SPPS). A **resin** is used to attach the amino acids so that they are in a specific orientation. Initially, one amino acid is attached to the resin, then each amino acid in the chain is attached in turn, allowing the amide link to form before the next amino acid is added. When the polypeptide chain is complete, it is removed from the resin and allowed to fold into the protein shape. The resin acts like the ribosome in natural protein synthesis.

Artificial protein synthesis also allows incorporation of new amino acids that do not occur naturally. Every amino acid has two isomeric forms except for glycine. Remember that **isomers** have the same molecular formula but a different structure. In this case, the two isomers have a similar structure and are mirror images of one another – **stereoisomers**. However, if you place the two isomers over one another, they are not the same, unlike other objects that have a mirror image. This phenomenon is known as **chirality**.

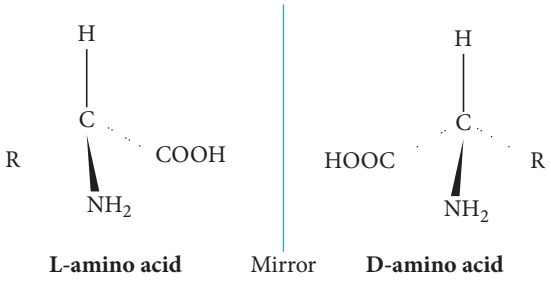
The best example of chirality is your hands. You have a left and a right hand and if you put one on top of the other with both palms down, they will not line up. If you put your left hand in front of a mirror, you will see a right hand in the mirror. This is a mirror image.

All natural amino acids are called L-amino acids, but they all also have a D form that is their stereoisomer. This can be seen in Figure C10.14.

In the pharmaceutical industry, the incorporation of D-amino acids is important in the production of drugs such as penicillin. The bacteria targeted by penicillin have a cell wall made of a polysaccharide and peptide units. The polypeptide starts with L-alanine and finishes with D-alanine. As the bacteria grow their cell wall, cross-links form between two peptide chains. Penicillin binds in place of the usual D-alanine molecule and causes disruption of these cross-links. As the cross-links do not form, the cell wall breaks down and the bacteria die. If an L-alanine molecule were present in the penicillin, then it would be unable to bind to this site because it is the wrong shape.

Even though the L and D isomers are very similar in shape, they do not always have the same properties. A famous example of this is the production and use of the drug thalidomide, which was given as a sedative to pregnant women in the late 1950s. Thousands of women gave birth to children with horrific birth defects due to this drug. The thalidomide molecule is a chiral molecule. One of the stereoisomers was a sedative, but the other isomer caused defects in the unborn foetus. When the drug was produced, both molecules were present in the medicine, causing a massive number of birth defects.

Figure C10.14 ▶
The L and D forms of an amino acid are mirror images (stereoisomers) of one another.



Solid black wedge indicates the attached functional group coming out of the page.

Dotted line indicates the attached functional groups/side chains are going into the page.

ACTIVITY 10.2

MODELLING CHIRAL MOLECULES

Aim

To model chiral amino acids and understand why they are not identical

You will need

- Molecular modelling kit with carbon, hydrogen, nitrogen, sulfur and oxygen atoms

What to do

1. Use Figure C10.9 to help you make a simple amino acid model (do not include glycine), such as alanine, valine, aspartic acid, lysine, serine and leucine.
2. Make a second, identical, amino acid and then swap the carboxylic acid and amine group.
3. Examine the models. Try to superimpose them, noting differences in their structures when in the same position.

What did you discover?

Draw your two molecules. By comparison with your three-dimensional models, explain why stereoisomerism is hard to represent on paper.

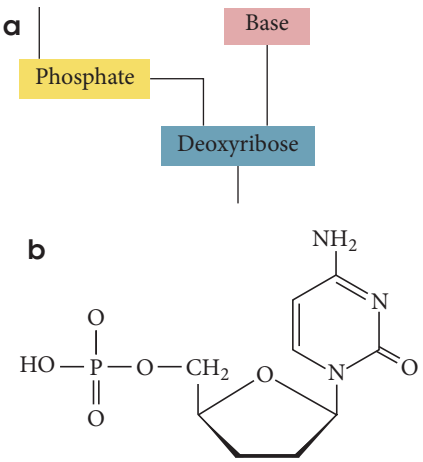
DNA nanotechnology

DNA nanotechnology is the use of **nucleic acids** to build structures that are then used in other areas of science and engineering. Using the structure of DNA in cells, where it carries genetic information, scientists have been able to build a range of devices that have had applications across medicine, engineering and materials production.

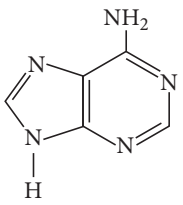
DNA structure

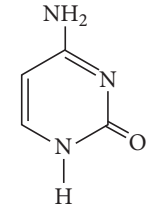
DNA stands for deoxyribonucleic acid. DNA has a very precise and ordered structure, which consists of a chain of nucleotides. A single **nucleotide** is shown in Figure C10.15. It contains a phosphate group, a deoxyribose sugar and a nitrogenous base.

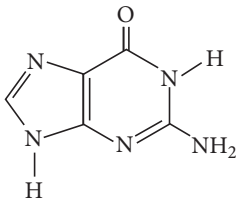
There are four **nitrogenous bases** found in DNA, as seen in Figure C10.16. Adenine (A) and guanine (G) are purines; thymine (T) and cytosine (C) are pyrimidines.

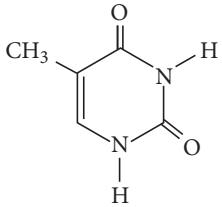


▲ **Figure C10.15**
A DNA nucleotide: a) simple structure and b) atomic structure


Adenine (A)


Cytosine (C)


Guanine (G)


Thymine (T)

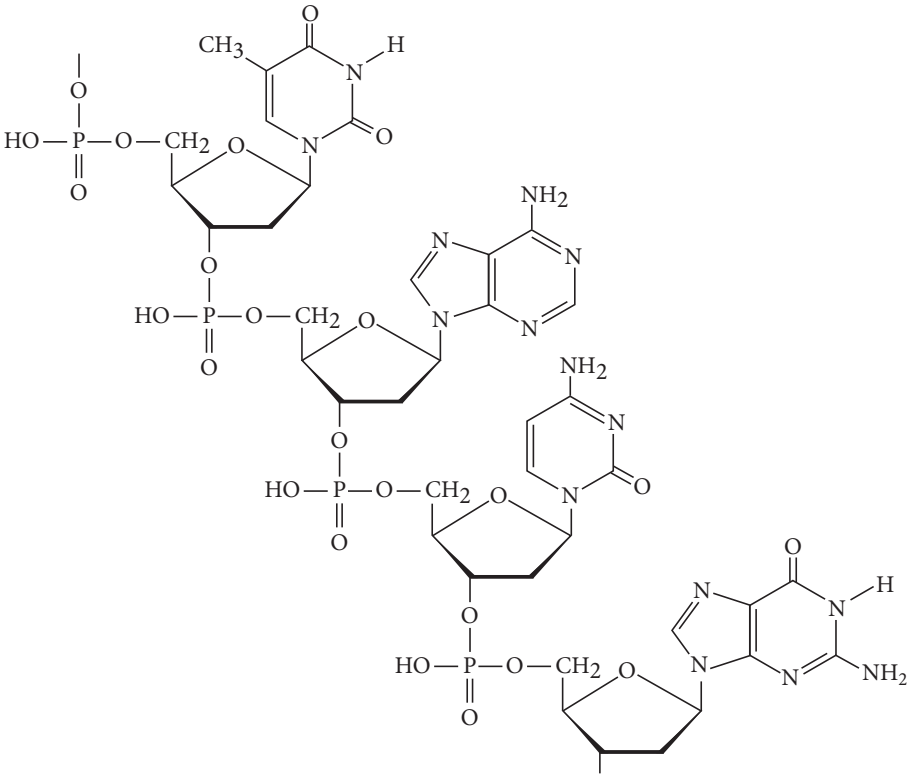
◀ **Figure C10.16**
The four nitrogenous bases in DNA



To see applications of this, refer to Context 6, 'Molecular manufacturing', page 126.

DNA is a chain of these nucleotides, as seen in Figure C10.17.

Figure C10.17 ▶
A section of a DNA molecule, showing nucleotides joined together

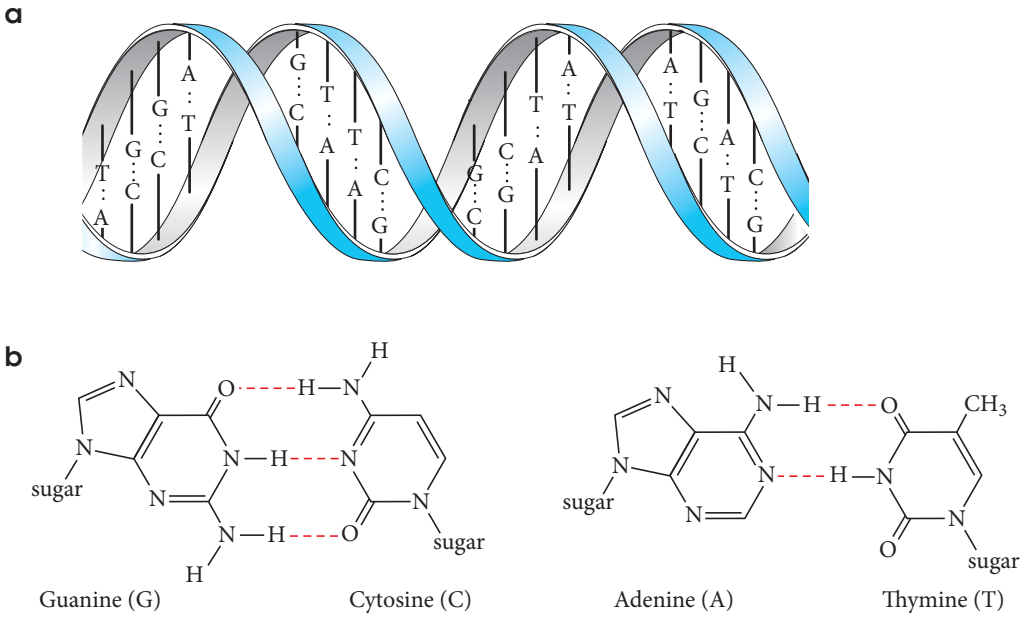


DNA HISTORY AND STRUCTURE

Use this interactive animation to learn about DNA structure and how it was discovered.

DNA has a double helix structure, as shown in Figure C10.18a. It is held in this shape by hydrogen bonds that form between the nitrogenous bases on two different strands of DNA. As you can see in Figure C10.18b, thymine and adenine pair up and form hydrogen bonds between them, as do cytosine and guanine. This complementary base pairing is fundamental to the structure of DNA. These two base pairings A–T and C–G always happen. Thymine cannot pair with cytosine or guanine, only with adenine. From Figure C10.18b, you can see that the structures of thymine and adenine allow the formation of two hydrogen bonds, while cytosine and guanine form three hydrogen bonds. If you lined up thymine and guanine, the sites for hydrogen bonding would not line up, so these two bases cannot join. In addition, the distance between adenine and thymine is the same as the distance between cytosine and guanine.

Figure C10.18 ▶
The DNA double helix is held together by hydrogen bonds between the bases of the nucleotides. a) The double helix structure; b) hydrogen bonding between base pairs. Dots and dashes represent hydrogen bonds.



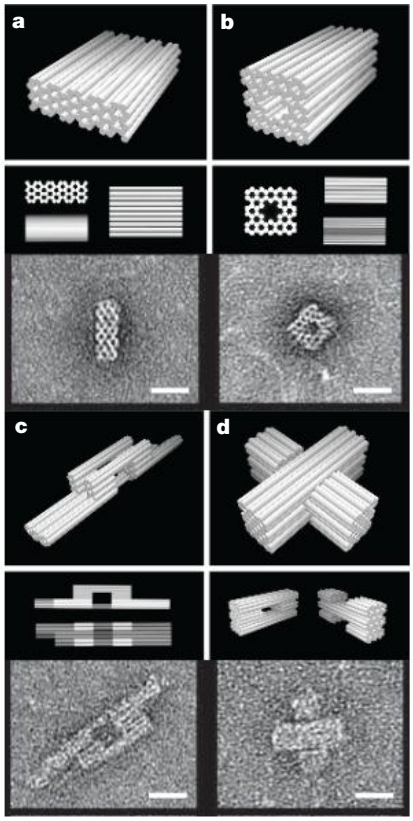
Artificial nucleic acid structures

Scientists can use the precise, ordered structure of DNA to produce artificial nucleic acid structures for uses outside its normal function as a carrier of genetic information. Scientists have been able to use nucleic acids to build two- and three-dimensional crystal lattices, nanotubes, molecular machines and DNA computers.

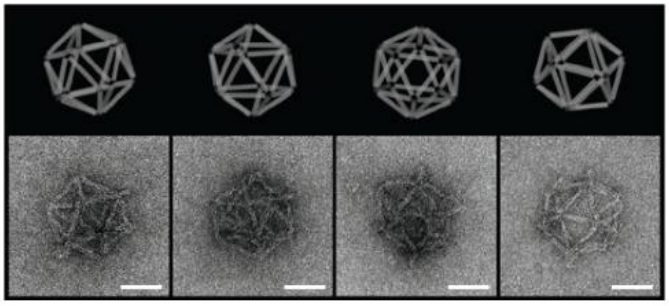
To create a particular structure, the systematic base pairing of DNA is used. As it only binds in certain pairings, if one strand of DNA is made with a specific set of bases, then it will 'grow' in a predictable way due to this base pairing. The sequence of bases determines the pattern of binding and thus the overall structure. The base sequences are designed by researchers so that when the base pairings occur, the structure has a set, desired shape.

DNA in a cell occurs in a double helix, as seen in Figure C10.18. When building these structures, the double helix is not useful, so other structures are made. Some of the structures are similar to scaffolding in a building, while some act like an enclosed basket to carry chemicals. Some of these structures can be seen in Figure C10.19.

One of the areas under development is the use of nucleic acids to build molecular robots. These robots, just like robots in industry, have a particular task. A molecular robot can be used to recognise a particular shape so can have applications in medicine where it could recognise diseased cells, viruses or specific bacteria. A molecular robot can be used to carry chemicals to a particular area of the body, again giving it a number of applications in medicine.



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▲ **Figure C10.19** DNA nanotechnology structures photographed using an electron microscope

WOW

DNA machines

Scientists have produced a spider out of DNA that is capable of walking across a surface, towards a target. The spider is a molecular machine designed to respond to the surface it walks across. The surface it is walking across is a highly folded piece of DNA.

The spider has legs that interact chemically with the DNA surface. To take a step, the legs break a DNA strand on the surface, which weakens the interactions between the spider and the surface. The spider then moves forward to where the interactions between itself and the surface are stronger. The spider is a DNA molecular machine that can sense the environment and respond to it.



Nicolle R. Fuller/Science Photo Library

▲ **Figure C10.20** A DNA spider 'walks' across a DNA molecule towards a target (in red).

Other scientists have developed a DNA machine that can pick up nanoparticles, useful as part of an assembly line to manufacture a larger structure, or in the human body to target toxic substances.

MASTERMINDING MOLECULES

Use this interactive to play a challenging game to create a new medicine by determining molecular shape and bonding.

QUESTION SET 10.2

Remembering

1 Define the following terms.
   - a Polypeptide
   - b Ribosome
   - c Chirality
   - d DNA

2 Amino acids are the basic unit of proteins.
   - a Draw the basic structure of an amino acid, labelling the amine, carboxylic acid and the R group.
   - b Explain how amino acids differ from each other.

3 Describe how protein synthesis occurs inside a cell.

4 Describe how artificial protein synthesis is used to grow proteins.

5 Explain the difference between L- and D-amino acid isomers.

Understanding

6 Explain the folding and bonding that leads to secondary and tertiary structures in a protein.

7 Explain, in terms of bonding, why specific DNA base pairings occur.

8 Explain the advantages of being able to control how DNA grows.

Applying

9 a Use the amino acids in Figure C10.9 to draw:
   - i a dipeptide that would result from the joining of alanine and leucine.
   - ii two dipeptides that could result from the joining of aspartic acid and valine.

   b Explain why there are multiple dipeptides that can form when two amino acids are joined.

Analysing

10 By considering the bonding that occurs when a protein is folded, explain why changes in the environmental temperature or pH cause the protein to unfold.

10.3 Bonding and atomic manipulation

Nanotechnology can be used to work with structures on the atomic scale. This is an example of the bottom-up approach to molecular manufacturing. When you can work with atoms individually and arrange or rearrange them exactly as you want them, then you can determine precisely what properties the final structures will have. Nanomaterials produced with this method can be stronger, lighter, water repellent, scratch resistant or resistant to damage from ultraviolet light. Properties such as flexibility, conductivity, microbial resistance and durability can be controlled. Thus, a material can be 'made to order' and have the exact properties required for the task it is designed for.

Supramolecular chemistry

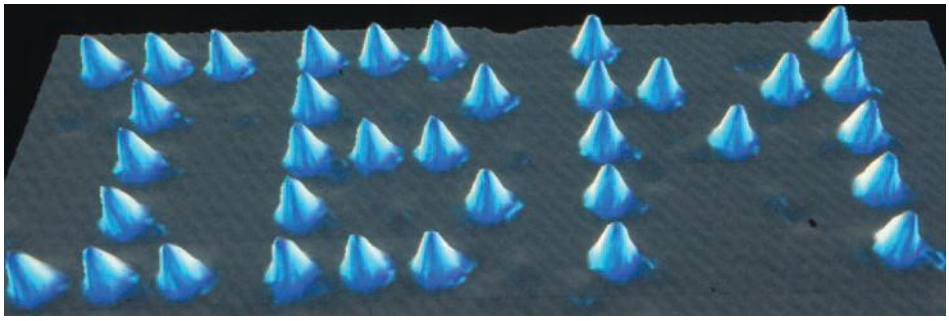
Supramolecular chemistry has a focus on the interactions between groups of molecules. In *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 6, you learnt about the weak intermolecular forces that occur between covalent molecules, including hydrogen bonds, dipole–dipole interactions and dispersion forces. This type of chemistry has led to the development of the technique **molecular self-assembly**. In this process, molecules are able to form specific structures without the influence of an outside source. It also allows for scientists to use **molecular recognition**. This occurs when molecules recognise specific molecules and will only react with or bond to those molecules.

WOW

Writing with atoms

To show how precise atomic manipulation technology can be, in 1989, the computer company IBM spelled out the company logo in atoms. They moved 35 xenon atoms on a background of copper atoms to spell out the letters IBM (Figure C10.21). This inspired competition among other scientists and researchers at Hitachi set a new record in 1991, by chiselling 1.5nm tall letters into a crystal.

A group of researchers at Stanford University decided to go one better. They used a microscope to move carbon monoxide molecules into an arrangement so there was a space in the middle of them. They then manipulated the electrons on the surface of the atoms to project a holographic image of letters in that space. Essentially, they were able to write in letters smaller than atoms.



Courtesy IBM Corporation

▲ Figure C10.21
The IBM logo written with xenon atoms on copper atoms

Both of these techniques have applications in medicine where molecules can recognise viruses or bacteria and lead to improved diagnosis of disease. They can also be used in materials production where structures that will bind to selective molecules or chemicals can be used in purification processes.

SELF-ASSEMBLING NANOPARTICLES

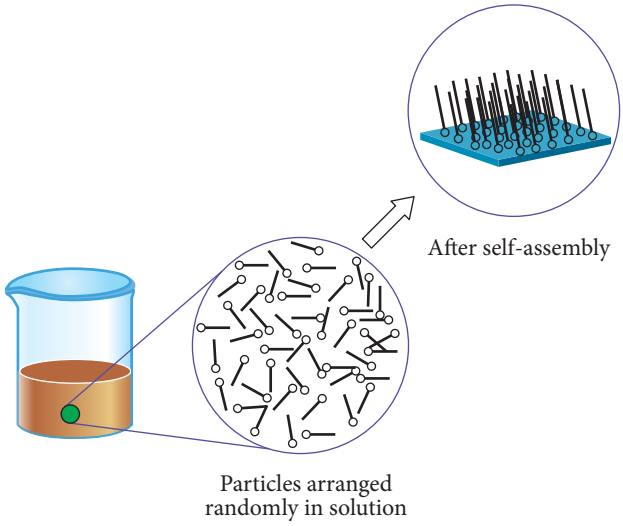
Watch this video of 12nm gold particles self-assembling.

Molecular self-assembly

Molecular self-assembly occurs through the formation of **secondary interactions** between molecules. The desired structure is programmed by placing functional groups in specific parts of a molecule. When they are near other molecules, the functional groups form secondary interactions such as hydrogen bonds as the functional groups line up perfectly.

The DNA nanotechnology described in section 10.2 that builds specific structures using nucleic acid–base pairing is an example of molecular self-assembly. Once the first strand is made; no outside interference is needed for the hydrogen bonds to form between the base pairs.

Nanotechnology-based self-assembly occurs when molecules are organised into a precise structure when an external stimulus is applied. The nanoparticles react to changes in temperature, or electric and magnetic fields. This allows the process to be controlled and to happen only when required. An example of nanoparticle self-assembly can be seen in Figure C10.22. This only occurs to the particles if they are nano sized due to their special properties.



▲ Figure C10.22
Self-assembly of nanoparticles in a solution

An application of this is the formation of a solid structure when heat or an electrical stimulus is applied. Materials can be flexible when the nanoparticles are disassembled, but heating causes the particles to self-assemble, making a more solid structure. The United States Army is using this to create 'instant' casts for broken bones.

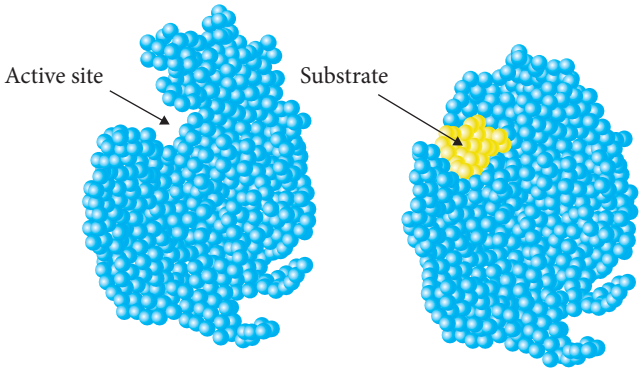


Figure C10.23 ▲
An enzyme and the binding site for its guest molecule

Molecular recognition

Molecular recognition occurs when two or more molecules interact through secondary bonding. One of the molecules is called the host molecule. It has bonding sites that will interact with a guest molecule. These bonding sites are the right size, shape and chemical structure to form bonds with the other molecule.

Enzymes and the molecules they work with are an example of **host–guest complexes**. The enzyme molecule has a region that has a similar shape to the guest molecule it needs to perform a function on. An example of this can be seen in Figure C10.23.

Scientists can use artificial protein synthesis and nucleic acid nanotechnology to build a host to bind to a very specific guest. One simple application of this is in water treatment, where host molecules are used to remove hazardous materials from the environment. They can be made in a variety of different sizes and shapes to bind with and thus remove a variety of different chemicals.

Another application is as a molecular sensor. This is sometimes called a **chemosensor** where the host molecule interacts with a substance to produce a change in the host molecule. This change can be measured and thus the presence and concentration of a guest chemical can be determined. This is useful for measuring levels of chemicals in the human body, water systems or in commercial products such as wine and perfumes.

ENZYME ACTION

Use this interactive activity to choose appropriate enzymes for a reaction and view their effect.

Nanotubes

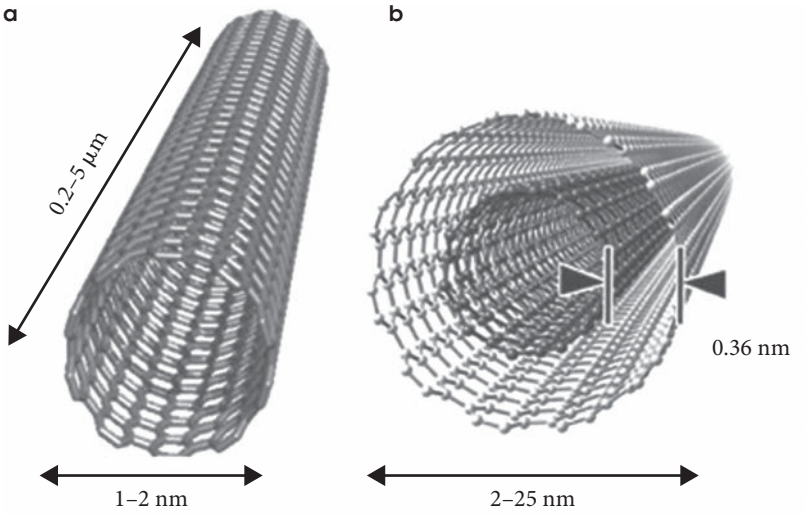
A **nanotube** is a tube that is constructed on the nano scale. It can be made from silicon, DNA or other materials, but the most common is carbon. A carbon nanotube is formed from sheets of **graphene**, covalently bonded carbon, with each sheet only one atom thick. The sheets are rolled into long tubes, and can be single walled, double walled or have a variety of other shapes.

How nanotubes are built

The best quality nanotubes are created by a method called arc-evaporation. A current is passed between two graphite electrodes, causing the graphite to vaporise. The vaporised graphite settles on the walls of the reaction vessel and on the cathode. The graphite on the cathode forms nanotube structures as the atoms settle and bond to each other.

Another method of producing nanotubes is to pass a carbon-containing gas, such as a hydrocarbon, over a **catalyst** containing nanoparticles of a metal such as iron, cobalt or nickel. These metal particles cause the hydrocarbon to break down into its component atoms. The carbon atoms then begin to grow into nanotubes.

To see how this is used in energy production, refer to Context 6, 'Molecular manufacturing', page 134.



a) © 2002 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany; b) Reprinted from Physica B: Condensed Matter, 323/1–4, Sumio Iijima, Carbon nanotubes: past, present, and future, pp. 1–5, 2002, with permission from Elsevier

Figure C10.24 ▶
a) Single-walled and b) double-walled carbon nanotubes

Both of these methods involve 'growing' the carbon nanotube atom by atom. This is an example of a bottom-up approach to producing nanomaterials.

To see how this is related to materials production, refer to Context 6, 'Molecular manufacturing', page 129.

Properties of carbon nanotubes

Carbon nanotubes are the strongest and stiffest materials yet discovered or made. A single carbon nanotube was tested to have a tensile strength equivalent to a mass of 6422 kg on a cable with a cross-sectional area of 1 mm^2. As they also have a low density, this makes them ideal for structural purposes. Carbon nanotubes have been used to develop strong but flexible materials that are even being implanted into the human body as artificial muscles and bones.

One of the properties of carbon nanotubes that is most useful is their high electrical conductivity. This makes them useful in batteries and fuel cells to produce electricity. Other properties that can be designed in a particular nanotube include optical properties, such as reflection and transmission of light, and thermal conductivity so they can be used under high temperature conditions.

Nanoparticles

A nanoparticle is an extremely small particle that can be built from the bottom up by atomic addition and manipulation or top down by making substances smaller and smaller until the correct sized particles are reached. Nanoparticles are classified according to size. Coarse particles are 2500–10 000 nm in diameter, fine particles are 100–2500 nm in diameter and ultrafine particles are 1–100 nm in diameter.

Production of nanoparticles

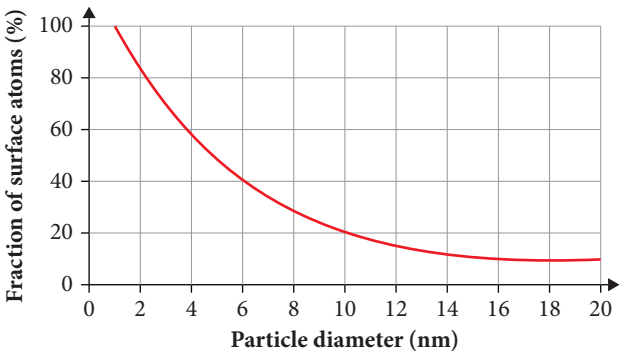
Many nanoparticles are made from larger particles of the same substance. Larger particles are crushed and ground into smaller particles, which are sorted by size and the nanoparticles collected. A different method involves **pyrolysis**, a process in which a gas is burnt at high pressure to form a solid. This solid contains nanoparticles, which are separated from the larger particles.

The Sol-Gel process uses a complex series of chemical reactions rather than extreme heat to produce nanoparticles. Small molecules are converted into solid materials by first converting particles into a colloidal solution (particles that are microscopically spread out in a solution), and then into separate nanoparticles. The end product can be in a thin film of bonded nanoparticles, a particle-based structure with a defined shape or a nanopowder with individual particles.

Uses of nanoparticles

There are two common uses for nanoparticles. The first is to create a uniform material. When larger particles of a substance are present, they pack in an irregular manner, leaving gaps between particles. This is a problem in the military or aerospace industries when high-quality ceramics, polymers and materials with dependable properties are required. Nanoparticles that can make a very uniform material is highly beneficial to these industries.

A second use relates to surface area. As the particles are smaller, there is an increased surface area available for reaction: 1 kg of 1 mm^3 particles has the same surface area as 1 mg of 1 nm^3 particles. Thus, you need a lot less of the substance to get the same catalytic effect from it. The main use for this is in catalyst chemistry.



▲ **Figure C10.25**
The effect of particle size on surface area

QUESTION SET 10.3

Remembering

1 Define the following terms.
   - a Molecular self-assembly
   - b Molecular recognition
   - c Nanoparticle

2 Describe the nanoproperties that allow molecular self-assembly to occur at the nanoparticle level.

3 Describe how an enzyme uses molecular recognition.

4 Explain why carbon nanotubes are useful.

5 Describe the methods used to produce nanoparticles.

Understanding

6 Explain how DNA nanotechnology uses the concept of molecular self-assembly.

7 Explain why the construction of carbon nanotubes is described as a bottom-up process.

8 Explain why surface area in nanoparticles is important in terms of collision theory and reaction rates.

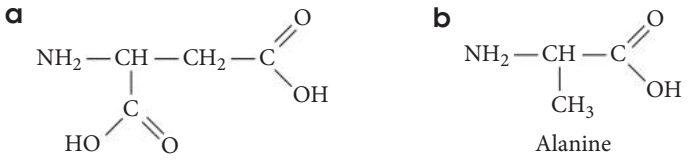
10.4 Protecting groups

A protecting group is temporarily added to a molecule to prevent a specific functional group from taking part in a chemical reaction. The use of a protecting group allows **chemoselectivity**, which is the ability to make a specific molecule or product over other possible products.

Preventing functional groups from reacting

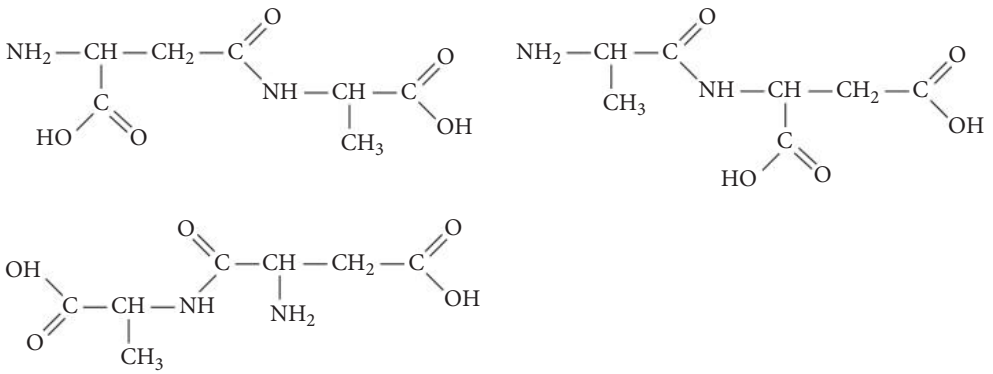
A simple example of the use of protecting groups is in the addition of two amino acids to form a dipeptide. If one of the amino acids has two carboxylic acid groups, then there are three possible dipeptides that can form. Figure C10.26 shows the amino acids aspartic acid, which has two carboxylic acid functional groups, and alanine.

Figure C10.26 ▶ Amino acids aspartic acid and alanine



The two carboxylic acid groups of aspartic acid mean that three possible dipeptides can form (Figure C10.27).

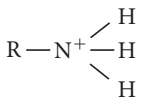
Figure C10.27 ▶ Three dipeptides that can form from aspartic acid and alanine



If you joined the two amino acids, then you would have each of the three dipeptides in the final product. This is because all functional groups are available to react. This creates a problem as each of the dipeptides has different properties. If you wanted to produce only one of the possible dipeptides so that your chemical had specific properties, then you would need to stop certain functional groups from reacting. This is the job of a protecting group.

Preventing unwanted side reactions

Another reason for using a protecting group is that some functional groups undergo unwanted side reactions in a reaction. For example, if an acid is used for a specific purpose, another functional group on the molecule might also react with the acid, causing a product to form that is unwanted. For example, a concentrated acid used as a catalyst for a reaction can react with an amine group to form a protonated amine, as seen in Figure C10.28. The protonated amine with a full positive charge has different properties from the amine functional group. A protecting group can be added to the amine while the reaction occurs, and then removed later on. This way, the amine never reacts with the acid.

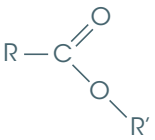
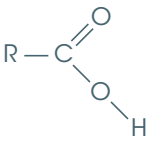
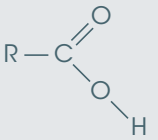
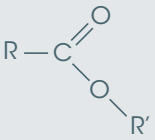
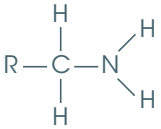
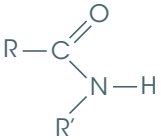
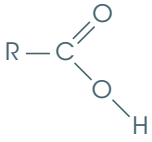


▲ **Figure C10.28** Addition of an acid to an amine group results in a protonated amine with very different properties.

Examples of protecting group reactions

The hydroxyl, or alcohol, functional group, the amine group and the carboxylic acid group are organic functional groups that are often protected. They are converted into less reactive functional groups such as esters or amides that will not undergo unwanted reactions. Table C10.1 summarises how these protecting group reactions occur.

Table C10.1 Summary of protecting group reactions

Functional group to be protected	Functional group to be converted into	Protecting reaction and chemical used	Reversal reaction
Hydroxyl or alcohol R′— O — H	Ester 	Carboxylic acid added in an esterification reaction 	Hydrolysis reaction by addition of water
Carboxylic acid 	Ester 	Alcohol added in an esterification reaction R′— O — H	Hydrolysis reaction by addition of water
Amine 	Amide 	Carboxylic acid added 	Reflux with strongly acidic or basic conditions



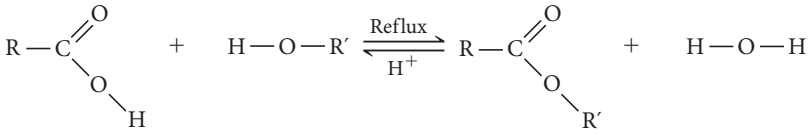
To see how this is applied, refer to Context 6, 'Molecular manufacturing', page 127.

Alcohol functional group protection

To learn more about ester production, refer to Chemistry section 6.9, page 310.

A common method of protecting an alcohol functional group is to temporarily convert it into an ester, as seen in Figure C10.29.

To form an ester from an alcohol, a carboxylic acid is added, along with a concentrated acid that acts as a catalyst, and the mixture is refluxed. **Reflux** is a process in which reactants are heated for an extended period of time without any loss of the reactants or products. The reaction mixture is heated, the evaporating gases move into a vertical condenser where the gases are cooled so they can return to the mixture. The equation for this reaction is:



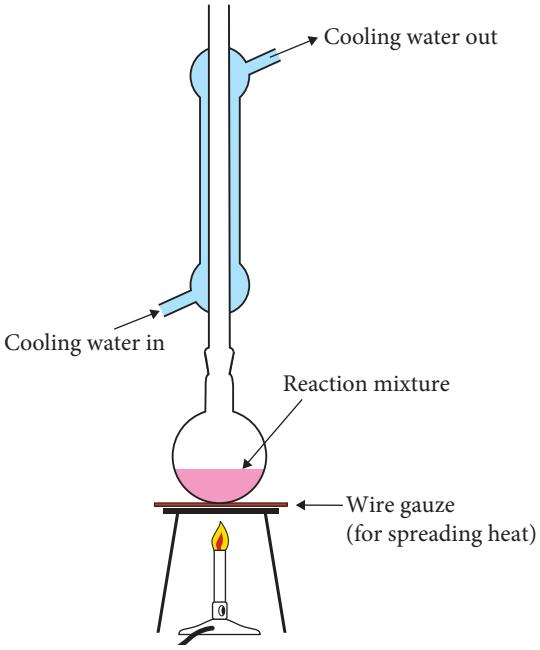
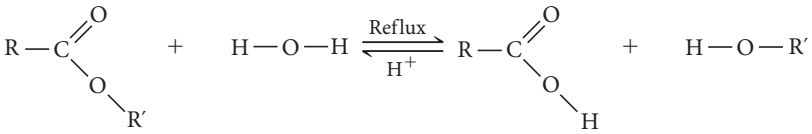


Figure C10.29 ▲
Reflux apparatus used to form and hydrolyse an ester

The ester that is formed will not react in the same way as the alcohol functional group, so the alcohol functional group is said to be protected.

To reverse the process, the ester is refluxed with concentrated acid and the reaction is reversed, producing the original alcohol. This process requires water and is called a **hydrolysis** reaction. Hydrolysis of an ester is shown in Figure C10.30.



▲ Figure C10.30
Hydrolysis of an ester

The protection of the carboxylic acid functional group uses the same chemistry as the protection of an alcohol.

Amine functional group protection

To protect an amine, an amide functional group is formed. An amine group is added to a carboxylic acid to form the amide functional group. The reaction is shown in Figure C10.31.

The amide functional group will not react and the original amine group is protected.

Amides are difficult to return to the original amine and carboxylic acid. Strong acids and bases need to be used, along with reflux in order to return to the original functional group. The acid hydrolysis and alkaline hydrolysis reactions are shown in Figure C10.32.

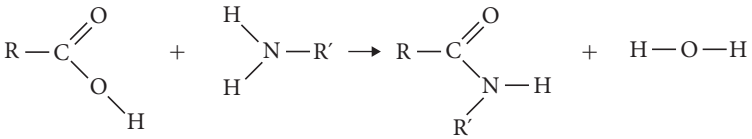
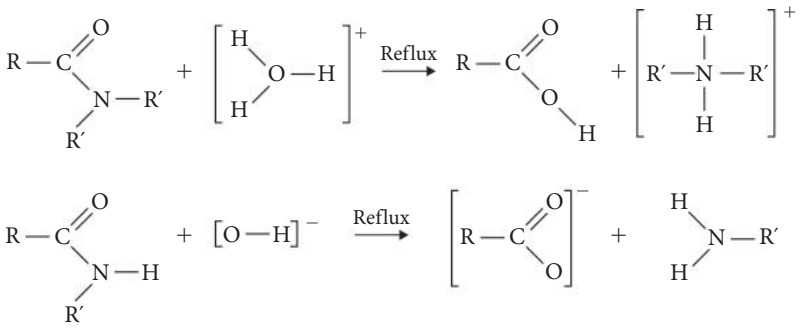


Figure C10.31 ▶
Protection of an amine group by formation of an amide

To learn more about amide production, refer to Chemistry section 6.10, page 316.



◀ **Figure C10.32**
Acid hydrolysis and alkaline hydrolysis of amides

QUESTION SET 10.4

Remembering

1 Define 'protecting group'.

2 Describe how a carboxylic acid functional group can be protected. Include a chemical that could be added to protect the group and any reaction conditions necessary for this to occur.

Understanding

3 The amino acid aspartic acid often needs protecting groups whereas glycine usually does not. Explain why this is the case.

Applying

4 The amino acids aspartic acid and isoleucine need to be joined so that the carboxylic acid on the isoleucine joins to the amine on the aspartic acid to form a dipeptide.
   - **a** Draw a diagram of both amino acids, identifying the functional groups that should react.
   - **b** Identify and explain how you could protect the other functional groups on the molecules.

5 Using Figure C10.9, write an equation to show how the following amino acid side chains might be protected.
   - **a** The hydroxyl group on serine by addition of ethanoic acid
   - **b** The amine group on lysine by addition of propanoic acid

Analysing

6 Suggest a reason why having unwanted molecules in the final product may be dangerous.

7 Certain amino acids are sensitive to pH changes and require protecting groups to prevent unwanted side reactions. Using Figure C10.9, identify two amino acids that might be sensitive to unwanted side reactions when acids and bases are present. Explain why you chose these amino acids.

CHAPTER CHECKLIST

You should know:

- molecular manufacturing is the production of molecules and other chemical structures with a specific shape or chemical composition
- substances have different properties on the macro and nano scale. These properties can be used to make materials with unique and special properties
- molecular manufacturing uses many methods, including the orientation effect, manipulation of atoms and using protecting groups
- the top-down approach breaks down larger substances while a bottom-up approach involves building the structure using atomic addition and bonding manipulation
- mechanosynthesis or the orientation effect is the lining up of reactive sites or functional groups on molecules so the final product has a specific structure
- protein synthesis is the joining of amino acids to form a polypeptide chain, which is folded in specific orientations to form the final protein. Folding of chains involves bonding between the amide groups within the chain and the R groups of the amino acids
- ribosomes are molecular machines that orient the amino acids so that they join in the correct sequence and orientation. Artificial protein synthesis mimics the action of a ribosome through use of a resin that holds amino acids in the correct orientation
- chirality exists in amino acids. The L and D isomers of an amino acid have different chemical properties, some of which are useful, some are harmful
- DNA nanotechnology uses nucleic acids to build useful structures. The precise orientation and bonding of nucleotides and DNA bases allows construction of a structure with a specific shape.
- molecular robots are built of DNA and can be used to recognise particular molecules or structures. This has many applications in the medical field
- nanomaterials with specific properties can be produced by building chemical structures through use of atomic manipulation and bonding
- molecular self-assembly and molecular recognition rely on intermolecular forces between molecules to recognise and form structures with other molecules. Enzymes and antibodies only bind molecules with specific shapes and functional groups
- carbon nanotubes are built atom by atom and have a structure that gives them extreme strength for their density and extraordinarily high conductivity
- nanoparticles have a high surface area and are useful in industrial applications such as production of catalysts
- a protecting group adds to a molecule temporarily to prevent a specific functional group from reacting. This means a specific molecule is formed, and/or unwanted side reactions do not occur. This is also called chemoselectivity
- simple esterification and condensation reactions to form esters and amide groups can be used to protect alcohol, carboxylic acid and amine groups.

You should be able to:

- identify an amino acid from its structure
- draw the dipeptides and polypeptide chains that form from the addition of amino acids
- write equations to show how alcohol, carboxylic acid and amine groups can be protected by ester and condensation reactions.

CHAPTER GLOSSARY

alpha helix secondary spiral protein structure held together by hydrogen bonds between the amide functional groups in the polypeptide chain

amino acid monomer of a protein containing a carboxylic acid and amine functional group and an R group that may be polar, non-polar or ionic

antibodies proteins that recognise specific-shaped molecules and structures and bind to them; they help to fight disease in living organisms

beta-pleated sheet secondary protein structure formed from two polypeptide chains held together by hydrogen bonds between the amide functional groups in the polypeptide chains

bottom-up approach molecular manufacturing starting with atoms and building up the desired structure by addition of atoms and manipulation of bonding

catalyst a substance that increases the rate of a chemical reaction by providing an alternative pathway with a lower activation energy

chemoselectivity the ability to produce one specific chemical product when several different chemicals can be the result of a reaction

chemosensor a molecule that can detect, indicate the presence of, and measure the concentration of a specific molecule or chemical

chirality a phenomenon where isomers have a non-superimposable mirror image

dipeptide a molecule formed by the joining of two amino acids in a condensation reaction by a peptide link

DNA replication the process of copying of the DNA in cells

enzyme a protein that catalyses chemical reactions in living organisms by orienting molecules in the correct manner and lowering the activation energy

functional group a special atom or group of atoms present in the families of organic compounds that imparts particular chemical and physical properties

graphene an allotrope of carbon in a two-dimensional sheet that can be shaped into a variety of shapes such as nanotubes

host–guest complex two molecules that fit together due to their specific chemical structure and molecular shape

hydrolysis the splitting of a molecule by addition of water, the reverse of a condensation reaction

isomers molecules with the same molecular formula, but with a different structure

mechanosynthesis another name for the orientation effect where specific functional groups or reactive sites are made to react together to produce the desired molecule

messenger RNA a molecule of RNA that is a copy of the DNA code so protein synthesis can occur

molecular manufacturing production of chemicals with specific shapes or chemical composition

molecular recognition molecules recognise molecules by their shape or bonding and can selectively bind to these specific molecules

molecular self-assembly molecules are influenced by an outside factor such as a magnetic or an electric field or can spontaneously form a specific structure through formation of bonds between atoms or molecules

nanomachine an artificially created protein designed to perform a specific mechanical task

nanometre one-billionth of a metre, or 10^{-9} m

nanoparticle a particle with size around 1–100 nm, often with specific and useful properties

nanotechnology science and engineering that occurs on the nanoscale, around 1–100 nm

nanotube commonly made of carbon, a one-atom sheet of covalently bonded atoms rolled into a nano-sized tube

nitrogenous base a base found in DNA and RNA

nucleic acid an organic molecule, such as DNA and RNA, made of chains of nucleotides

nucleotide composed of a nitrogenous base, phosphate group and a deoxyribose or ribose sugar, they join together to create DNA or RNA respectively

orientation effect positioning of molecules prior to reaction so functional groups or reactive sites on the molecules line up, giving a specific final product

photosynthesis the process whereby organisms, particularly green plants, can use sunlight to produce nutrients (sugars) from carbon dioxide and water with the use of light energy

polypeptide a long chain of amino acids that folds into secondary and tertiary protein shapes through the use of intermolecular forces

protecting group a part of a molecule that temporarily forms to prevent a functional group from reacting

protein synthesis joining of amino acids to form chains, which fold in specific orientations to form a protein

protonate addition of a proton to a functional group, usually resulting in a positively charged functional group

pyrolysis a process of decomposition of a substance at high temperatures

reflux process of extended heating of a mixture without any loss of reactants and products

resin material used in the production of artificial proteins, holds the amino acids in the correct orientation so they join in the desired manner

respiration the conversion of sugars into carbon dioxide and energy in living organisms

ribosome a natural molecular machine that produces proteins through protein synthesis

secondary interactions bonds that occur between molecules, including hydrogen bonds, dipole–dipole interactions and dispersion forces, also called intermolecular forces

stereoisomers isomers that are a mirror image of each other

supramolecular chemistry chemistry focusing on the interactions between groups of molecules

top-down approach molecular manufacturing starting with larger substances and breaking them down into smaller, more useful substances

transfer RNA moves amino acids into place so they can be joined in a ribosome during protein synthesis

yield the amount or percentage of the possible product that is actually produced

CHAPTER REVIEW QUESTIONS

Remembering

1 Explain why it is important for large molecules to be in the correct orientation to have an efficient reaction.
2 Identify the two functional groups found on an amino acid and write an equation to show how two generic amino acids (just use R for the side group) can join to form a dipeptide.
3 Explain why an amino acid can be a chiral molecule.
4 State which DNA bases form pairs. Explain why only these pairings occur.
5 Describe how an artificial DNA structure can be made.
6 Describe how molecular self-assembly creates structures when an external change is made to the environment.
7 Identify the properties of carbon nanotubes that make them so useful.

Understanding

8 Explain why materials and chemicals produced using nanoparticles and nanostructures are so useful.
9 Using Figure C10.9, explain why joining glycine and alanine will only result in two different dipeptides while joining valine and aspartic acid will result in three different dipeptides.
10 Create a flowchart to show the formation of a protein from amino acids through secondary, tertiary and quaternary structures. Include the type of bonding that forms at each stage.
11 Explain why the bonding that forms between the R groups in the tertiary protein structure can vary in strength.
12 Nanoparticles have a high surface area. Explain why this is useful in terms of collision theory and rates of reaction.
13 Explain, using an appropriate amino acid structure from Figure C10.9, how a protecting group can prevent an unwanted side reaction.

Applying

14 Using Figure C10.9, identify two amino acids that have R groups that can form:
   a hydrogen bonds with other R groups.
   b an ion under acidic or basic conditions.
15 Using Figure C10.9, draw all possible dipeptides that can form from:
   a leucine and alanine.
   b asparagine and valine.
16 Refer to the structure of aspartic acid in Figure C10.9. Use an equation and include all reaction conditions to show how the second carboxylic acid could be protected using an esterification reaction.
17 Refer to the structure of lysine in Figure C10.9. Use an equation to show how the amine on the R group could be protected using a condensation reaction.

Analysing

18 Top-down and bottom-up approaches are used to create nanoparticles and nanostructures.
   a Suggest reasons why a top-down approach uses more energy considering the methods used.
   b Suggest drawbacks to using a top-down approach.
19 Suggest how molecular self-assembly could be used as a chemical sensor to detect changes in temperature.
20 Suggest a possible negative outcome that could arise from molecules joining in the incorrect orientation.

CHAPTER 11 SCIENTIFIC INVESTIGATIONS

By the end of this chapter you will have covered the following material.

Science Inquiry Skills

- Identify, research and refine questions for investigation; propose hypotheses; and predict possible outcomes (ACSCH074 and ACSH112)
- Design investigations, including the procedure/s to be followed, the materials required, and the type and amount of primary and/or secondary data to be collected; conduct risk assessments; and consider research ethics (ACSCH075 and ACSCH113)
- Conduct investigations, including using volumetric analysis techniques and constructing electrochemical cells, and including using organic synthesis methods and collating data from chemical analyses, safely, competently and methodically for the collection of valid and reliable data (ACSCH076 and ACSCH114)
- Represent data in meaningful and useful ways, including using appropriate graphic representations and correct units and symbols; organise , process and analyse data to identify trends, patterns and relationships; identify and distinguish between random and systematic errors, and estimate their effect on measured results; discuss how the nature of the procedure and the sample size may influence uncertainty and limitations in data; and select, synthesise and use evidence to make and justify conclusions (ACSCH077 and ACSCH115)
- Interpret a range of scientific and media texts, and evaluate processes, claims and conclusions by considering the quality of available evidence, including confidence intervals in secondary data; and use reasoning to construct scientific arguments (ACSCH078 and ACSCH116)
- Select, construct and use appropriate representations, including half-equations, balanced chemical equations, equilibrium constants and expressions, pH, oxidation numbers, standard electrode potentials and cell diagrams; and physical, virtual and graphical models of primary, secondary and tertiary structures, structural formulas, chemical equations, systematic nomenclature (using IUPAC conventions) and spectra, to communicate conceptual understanding, solve problems and make predictions (ACSCH079 and ACSCH117)
- Select and use appropriate mathematical representations to solve problems and make predictions, including calculating cell potentials under standard conditions, using the mole concept to calculate moles, mass, volume and concentrations from volumetric analysis data, determining the yield of incomplete reactions, and calculating the pH of solutions of strong acids and bases (ACSCH080)
- Select and use appropriate mathematical representations to solve problems and make predictions, including using the mole concept to calculate quantities in chemical reactions, including multi-step reactions, and the percentage yield of synthesis reactions (ACSCH118)
- Communicate to specific audiences and for specific purposes using appropriate language, nomenclature, genres and modes, including scientific reports (ACSCH081 and ACSCH119)

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11.1 Introduction

Performing investigations is your chance to experience what doing science is really like. Science is about finding things out through observation and experiment, which is what doing investigations is all about. This is why investigations are central to science, *and* why they are so much fun.



Science Photo Library/Phil Boorman

Figure C11.1 ▲ Students conducting an investigation on the acidity of soft drinks

Sometimes, an important advance in science begins with a casual observation or a lucky accident. This happened in 1799, when Alessandro Volta produced electricity from alternating discs of copper and zinc separated by material soaked in acid. This led to further inquiry, which allowed scientists to understand how a chemical reaction can produce electricity, which has led to the development of the variety of batteries available today.

Scientific investigations can take years to complete and may involve collaboration among many scientists. They may require access to special equipment in Australia or other countries. They may cost a lot of money, sometimes millions of dollars, to complete. Hence, scientists invest time in *planning* investigations before they begin. When scientists apply for grants to carry out investigations, they need to show that they have carefully planned what they will do and how any money provided will be spent. Good planning is crucial to the success of the investigation.

Scientists then make careful *measurements and observations* and record their *results*. They *keep records* of all their experiments. This is a legal requirement. Typically, experimental results need to be kept for 5–7 years. There are also requirements on how and where data are stored.

Once collected, the data need to be *analysed*. There are various ways this is done, but in the physical sciences (physics, chemistry and geology), it almost always involves constructing graphs. Once a relationship is established graphically, a mathematical relationship can be derived.

Finally, the results of the investigation must be *communicated*. Usually this involves publishing a scientific paper in either a journal or conference proceedings. It often includes presenting the results in talks or posters at conferences. If the result is funded by a grant, then a research report must be submitted. If the results are really exciting, then the scientists may write a media release. However the results are communicated, this step must happen for the investigation to be completed.

When *you* perform scientific investigations, you will also need to plan carefully. You will find out about the topic by reading about what other people have done. You will collect data from your own experiments and secondary sources. You will then analyse that data and draw conclusions about what it means. Finally, you will communicate your findings. Each of these steps is outlined below.

11.2 Planning your investigation

There are many things to consider when planning an investigation. You need to think about how much time you will have inside and outside class. You will also need to think about what space and equipment you will need and where you will go if you want to make measurements or observations outside.

You may be working in a group or on your own. Most scientists work in groups. If you can choose who you work with, think about it carefully. It is not always best to work with friends. Think about working with people who have skills that are different from your own.

Finally, and probably the first thing that most students think about, is the topic of the research. You will need to come up with a **research question** or **hypothesis**.

Choosing a research question

Obviously, it is a good idea to investigate something that you find interesting. If you are working in a group, try to find something that everyone in the group finds interesting.

A good way to start is by 'brainstorming' for ideas. This works whether you are working on your own or in a group. Write down as many ideas as you can think of. Don't be critical at this stage. If you are working in a group, get everyone to contribute and accept all contributions uncritically. Write down all ideas.

After you have run out of ideas, it is time to start being critical. Decide which questions or ideas are the most interesting. Think about which of these it is possible to investigate given the time and equipment available. Make a shortlist, but keep the long list too for the moment. Once you have your shortlist, it is time to start refining your ideas.



Alamy/Jim West

▲ **Figure C11.2** Brainstorm as many ideas as you can in your group.

Researching and refining your question

The next step is to find out what is already known about the ideas on your list. Use the Internet, your textbooks and the library to find out. Make sure you *keep a record* of the information that you find as well as *the sources*. You should start a **logbook** at this stage. You can write in references, or attach printouts to your logbook. This can save you a lot of time later on! Many research students forget to do this when they first start reading about their topic and then have to search all over again.

Good record keeping is important in scientific research, and it begins at this stage of the investigation.

Be critical of what you read. Do not assume that everything you read online or even in books is true. Try to find **reliable** sources of information. Textbooks, websites from universities and government research agencies are usually very reliable. Publications and webpages from professional associations, such as the Royal Australian Chemical Society and equivalent international organisations are also good sources. Blogs and homepages of other students are not usually reliable, although they are useful to give you ideas. Be sceptical about websites that are trying to sell you something. Talk to your teacher about sources of information as well. They will be able to tell you if a website is reliable, and suggest sites that they know are suitable.



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▲ **Figure C11.3** Start researching your topic and make sure you keep a record of all your references.

LEARN CHEMISTRY

Visit this website for many ideas for experiments in chemistry.

You may find examples of similar investigations to the one you are thinking of. It is a good idea to look at these, so you can learn from the experience of other researchers. However, in general, it is better not to try to replicate someone else's investigation exactly. If you do decide to replicate someone else's investigation, then you must acknowledge and carefully **reference** their work. See the section on References on page 475. If you do not do so, then it is **plagiarism**. This is a very serious form of academic misconduct. Talk to your teacher about how original your research needs to be, how closely it can be based on someone else's work and the correct way to acknowledge the contributions of others. It is much better to do this at the start than to be accused of cheating later on!

Finally, talk to your teacher about your ideas. They will be able to tell you whether your ideas are likely to be possible given the equipment available. They may have had other students with similar ideas and can make suggestions.

After you have researched your questions and ideas, you should be able to narrow down the shortlist to the one question that you want to tackle. If none of the questions or ideas looks possible (or still interesting), then you need to go back to the long list.

Proposing a research question or hypothesis

Once you have decided on what you will investigate, you need to turn it into a research question or a hypothesis.

A research question is one that can be answered by performing experiments or making observations. A hypothesis is a prediction of the results of an experiment, which can be tested by performing experiments or making observations.

Research questions

A research question may be of the form 'How does the temperature of a solution affect how quickly a reaction occurs?'. The aim of your research is then to answer the question.

You need to frame the question carefully. It needs to be specific enough that it guides the design of the investigation. A specific question rather than a vague one will make the design of your investigation much easier. Asking 'Will a reaction occur more quickly if the temperature is higher?' tells you what you will be varying and what you will be measuring. It also gives a criterion for judging whether you have answered the question.



Corbis/Frederic Cirou

Figure C11.4 ▶ Your research question will guide your investigation. These students are finding out how temperature affects the rate of a reaction.

Asking 'What will make a reaction occur the best?' is not a good question. This question does not say what will be varied, nor does it tell you when you have answered the question. 'Best' is a vague term. What you mean by 'best' may not be what someone else means.

A good research question identifies the **variables** that will be investigated. Usually you will have one **dependent variable** and one **independent variable**. For a lengthy investigation, you may have two or more independent variables. Variables are discussed in more detail on page 460.

Finally, a good research question should be answerable with the time and equipment available.

Hypotheses

A hypothesis is a tentative explanation or prediction, not yet confirmed by experiment, such as 'As the temperature of the sodium thiosulfate solution increases, the rate of the reaction with hydrochloric acid will increase'. Your hypothesis should give a prediction that you can test, ideally quantitatively.

A hypothesis is usually based on an existing **model** or **theory**. It is a prediction of what will happen in a specific situation based on that model. For example, collision theory is used to describe what happens during a chemical reaction. This can be used to develop a hypothesis regarding factors that affect the rate of a reaction, including temperature.

A hypothesis should give you a prediction that you can test by performing an experiment. This means it should at least be **falsifiable** (can be proven false). A good hypothesis should be able to be disproved. However, you will *not* generally be able to claim that you have proved your hypothesis.

If your experiments agree with predictions based on your hypothesis, then you can claim that they support your hypothesis. This *increases your confidence* in your model, but *it does not prove that it is true.* Hence, an aim for an experiment should not start 'To prove …', as it is not possible to actually prove a hypothesis, only to disprove it.

If your experimental results disagree, then you may have disproved your hypothesis. This is *not* a bad thing! Often the most interesting discoveries in science start when a hypothesis based on an existing model is disproved. This means that the model it was based upon is either not a good model, or does not apply to the particular situation. You could then try to work out why the model does not apply, or try to formulate a better model. What to do when your hypothesis is not supported is discussed further in section 11.4 on page 472.

In summary, a good research question is a question that is specific and can be answered by performing experiments and making measurements. A good hypothesis is a statement that predicts the results of an experiment and can be tested using measurements.

Even if your question or hypothesis meets these criteria, do not be surprised if you change or modify it during the course of your investigation. In scientific research, the question you set out to answer is often only a starting point for more questions.

Designing your investigation

Once you have a specific research question or hypothesis, you need to design your investigation. It is fun to start making measurements or observations immediately, but it is also important to spend time learning how to use the equipment, and experimenting to find the best way to set up your investigation. You may also discover that you need different or more equipment. This may save you time later on.

It is also important to keep focused on the purpose of your investigation. At the end of the process, you need good data that answer your question or test your hypothesis. Having a plan

helps to ensure that you will take the measurements you need. The longer the investigation, the more important it is that you have a clear plan. There are several things to consider:

- What data will you need to collect?
- What materials and equipment will you need?
- When and where will you collect the data?
- If you are working in a group, who will collect the data?
- Who will be responsible for record keeping?
- How will the data be analysed?

The data that you collect will always include **secondary data**, and will usually include **primary data**. Secondary data are data that have been collected by someone else.

You will already have collected some secondary data when you investigated your research topic to formulate your question or hypothesis. You will probably want to collect more secondary data. If your topic is not one for which you can collect primary data, then you will need to rely on secondary data. Remember that when you collect secondary data, it is important to use reliable, reputable sources.

Primary data are data that you collect yourself. You can collect data by performing experiments. In chemistry, primary data include measurements such as temperature, mass, volume and time. You should also make observations such as colours, smells, sounds and other changes that you can see. You will have had practice at measuring some or all of these things already. You need to decide which variables you will measure and which variables you will control. Consider which variables you can control, and which you cannot.

Consider how you will analyse the data. Will you need access to specific software such as a graphing or statistics package? If so, make sure that you know how to use it. If you are using software to draw graphs, then you need to know how to produce a scatter graph and draw a **line of best fit**. Note that a line of best fit is *not* the same as joining the dots. You should *never join the dots*, even though this is often the default setting in spreadsheet software. You should consult a reference guide or the 'help' menu for your software, or ask your teacher. Graphs are discussed in more detail in section 10.4 on page 411.

Keep a record of your planning. This should go in your logbook. Writing down what you plan to do, and why, will help you stay focused during the investigation. If you are working in a group, then dividing the tasks and keeping a record of what each person agrees to do during the investigation will help to coordinate the project.

Variables and measurements

Variables are anything that may change the results of an investigation or experiment. For each investigation, the variables can be classified as independent, dependent or controlled variables.

The independent variable is what you change. For example, in the investigation to determine the effect of temperature on the rate of a reaction, you would change the temperature. Therefore, the temperature is the independent variable.

The dependent variable is what you are measuring or finding out. In the temperature and reaction rate investigation, you are measuring the reaction rate. Therefore, reaction rate is the dependent variable.

Your hypothesis should clearly show your predicted relationship between the independent and dependent variables. For example, 'As the temperature increases, the reaction rate will increase'.

It is important that everything else that may affect the results is kept constant. Therefore, all other variables must be controlled. Your method should clearly show how you are controlling these variables. For example, you should describe what volume and concentrations of solutions you are using, whether you are stirring the solutions, when timing will start and stop, what size flasks you will use and so on. If these variables change as well as the independent variable, then you would not be able to tell which variable caused the change in the dependent variable. For example, if you had changed the concentration and temperature of the solution, then which one caused the increase in the reaction rate?

In most investigations, there will only be one independent variable. However, in a longer investigation, it is possible to investigate the effect of more than one variable. In this case, it is

important to plan carefully so that each set of data has only one variable changed. For example, if you were going to investigate the effect of concentration and temperature on the rate of a reaction, then you would test a variety of concentrations at one particular temperature, then repeat the process at the next temperature and so on. This way you can clearly see the effect of concentration and the effect of temperature separately.

When variables have a numerical value, you make **quantitative measurements**. You measure that numerical value in the appropriate units. For example, you may measure temperature in degrees Celsius, mass in grams or volume in litres.

Continuous variables may take any possible value, usually within some range. Length, time, mass, temperature and volume are examples of continuous variables used in chemistry. A variable that may take only fixed values is called a **discrete** variable. Often these are whole numbers of things that cannot be broken into smaller parts, such as electrons, protons or atomic number.

In some investigations, you may use **qualitative** measurements or data, which are descriptions such as colour, formation of a precipitate or presence of bubbles. For example, a chemical reaction may lead to a colour change. You would usually describe the colour in words, such as 'pink' or 'green', rather than using a number. Sometimes you use a combination of qualitative and quantitative data.

Once you have decided on the variables you will be measuring, you will be able to identify the equipment and other resources you will need.

Identifying the resources required

Now that you have decided on your hypothesis, you should consider what you will need to test your hypothesis. Make a list of all the materials and equipment that you will need.

- What chemicals will you need for your reaction? Be specific and include volumes, masses and concentrations where applicable.
- What equipment will you need to hold the chemicals? Include quantities and sizes or volumes of equipment such as beakers and conical flasks.
- How will you measure the chemicals? Include quantities and sizes or volumes of equipment such as pipettes and measuring cylinders.
- How will you change the independent variable?
- How will you measure the dependent variable?
- Have you chosen equipment that will allow accurate measurements?



Shutterstock.com/Dasha Petrenko

▲ **Figure C11.5**
Your equipment list should be thorough and detailed to include everything that you will need to conduct your investigation.

You must also consider the safety aspects of your experiment. Look up and print out the Material safety data sheets (MSDS) for the chemicals that you are using and include any safety equipment needed. You should also consider where the experiment will be conducted. Some reactions should only be carried out in a fume cupboard. Other, general, safety equipment such as safety glasses, aprons or labcoats and gloves should also be included in your equipment list.

As you develop your method, you may need to adjust your equipment list to ensure that it is thorough and detailed.

Planning the experimental procedure

The most common problem that students have when doing research is time management. It is important to plan to have enough time to perform the experiments, *and* to analyse them, *and* to report on them. You also need to allow time to learn how to use the equipment if you have not used it before.

Your procedure is what you are going to do in your investigation. This needs to clearly state what will be done at each step in as much detail as possible. As you are planning, consider the following questions.

- How many variations of your independent variables are you going to test? For example, how many different temperatures will you have?
- What are you using to measure each of the chemicals?

- What will you use to hold the chemicals?
- Will you stir the solution?
- How will you measure your dependent variable?

In your planning, ensure that you only change one thing – the independent variable. Everything else needs to be kept constant, and you need to show this will be achieved – for example, the volume and concentration of solutions will you use, the order chemicals are added, whether the solutions are mixed or not and when a stopwatch will be started and stopped.

Whenever possible, repeat your measurements, so allow time for this. This allows you to check that your measurements are **valid**. Valid results are affected only by a single independent variable. If the results are similar each time, then your results are likely to be valid. If a result is not **reproducible**, it is probably not a valid result. A result is reproducible if you make exactly the same measurement more than once and get the same result, within the limits of experimental uncertainty. If a result is not reproducible, then a variable other than the one you are controlling is affecting its value. If this is the case, you need to determine what this other variable is, and control it if possible.



Corbis/Frederic Cirou

Figure C11.6 ▲
Sometimes experiments just don't work.

Sometimes experiments do not go as planned. This is often due to other factors influencing the experiment. It is a good idea to do a trial run of your experiment to check that your procedure will work. You can then adjust your procedure as required before conducting all of your trial.

Make sure you allow time for analysis. Ideally, do as much analysis as you can while you collect results. If you plot graphs as you take measurements, then you will be able to identify **outliers** early. An outlier is a data point that does not fit the pattern of the rest of the data. If you identify an outlier while you still have access to equipment and space, then you can check the measurement and make sure that you didn't make a mistake.

After you have analysed your results, you need to write your report or communicate your findings in some other form. You need to plan ahead how this will be done. If you are working in a group, decide who will write which part of the report and when. Who will proofread it? Who will be responsible for making sure all the parts fit together?

You may find a timeline useful. A timeline helps keep you on track, and reminds everyone of their responsibilities. If you are working in a group, then get everyone to agree on it.

You can use the following table as a template.

Date and place	What will be done	Who will do it	Outcomes

Risk assessment

You may be required to complete a risk assessment before you begin your investigation. Even if this is not a requirement, it is a good idea to think about it. You need to think about three things:

1 *What are the possible risks* to you, to other people, to the environment or property?
2 *How likely is it* that there will be an injury or damage?
3 If there is an injury or damage to property or environment, *how serious are the consequences* likely to be?

A 'risk matrix', such as Table C11.1, can be used to assess the severity of a risk associated with an investigation. The consequences are listed across the top from negligible to catastrophic.

Negligible may be getting clothes dirty or a very minor injury such as a scratch. Marginal might be a cut from broken glass. Severe could be a more substantial injury or a burn. Catastrophic would be a death or the release of a toxin into the environment. When you are considering the risks involved with chemicals, read the MSDS for each chemical used or produced. (These are readily available on the Internet.)

In general, you need to ensure that your investigation is low risk. You can use a risk matrix either for individual identified risks, or for the investigation overall. If there are multiple experiments, then you would use a risk matrix for each one.

Table C11.1 Risk matrix for assessing the severity of risk

	Consequences			
Likelihood	**Negligible**	**Marginal**	**Severe**	**Catastrophic**
Rare	Low risk	Low risk	Moderate risk	High risk
Unlikely	Low risk	Low risk	High risk	Extreme risk
Possible	Low risk	Moderate risk	Extreme risk	Extreme risk
Likely	Moderate risk	High risk	Extreme risk	Extreme risk
Certain	Moderate risk	High risk	Extreme risk	Extreme risk

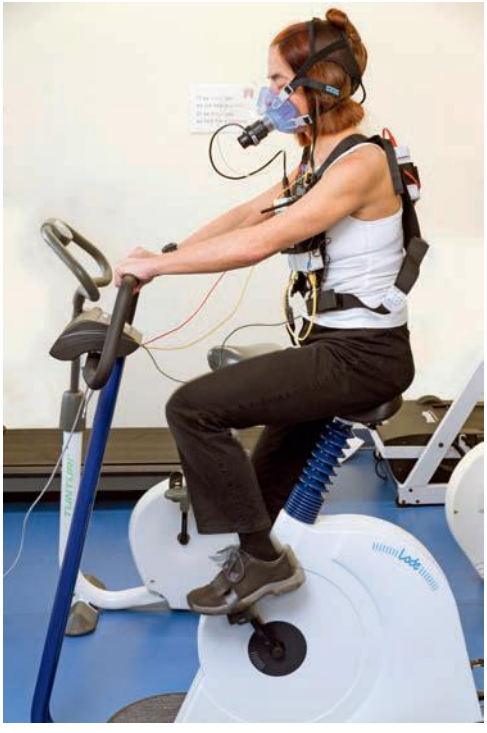
Once you have considered the possible risks, you need to think about what you will do about them. What will you do to minimise them, and how will you deal with the consequences if something does happen? This may be as simple as, 'Wear appropriate safety gear'. You can use a risk assessment table like the one shown.

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
2 mol L^{-1} HCl is corrosive to skin and clothes.	Clean up all spills immediately. Wear gloves, safety glasses and an apron.

Ethics

Ethics in research can be controversial. More than one scientist has lost their job for unethical research behaviour. Being ethical in your research has two aspects. The first is about being honest as a scientist. This means recording data accurately, and not ignoring, hiding or changing any data that do not support your hypothesis. It means acknowledging and referencing sources of information, including books, websites, articles and people who have helped you. It means not using other people's ideas or data without their knowledge and permission. Put simply, it is showing integrity or 'doing the right thing'. A good rule is that if you wouldn't want someone to know what you are doing, you probably shouldn't be doing it. It is no different from behaving ethically in any other area of your life.

The other aspect to ethics is treating animals, other people and the environment with care and respect. If your investigation



Science Photo Library/Antonia Reeve

◀ **Figure C11.7** When working with humans, you need to make sure that they are not harmed in any way.

NHMRC

You can find NHMRC human and animal ethics guidelines here.

will be using humans or animals, then you need to make sure you do not harm them, either physically or psychologically. If you are working with animals, then you need to make a strong case for any investigation that harms or could potentially harm them. When scientists want to use humans or animals in their research, they need to be able to show that the benefits to the environment, other animals or humans significantly outweigh the negative effects on the animals or humans used. The National Institute of Health and Medical Research (NHMRC) has guidelines on the ethical use of humans and animals in experimentation.

11.3 Collecting your data

Once you have planned what you are going to do, collected your equipment and set it up, it is time to start collecting data. This is usually the fun part of any investigation. Don't forget you have a question to answer or a hypothesis to test! To complete your research successfully, you need to make sure that you think carefully about what you do and keep good records.



iStockphoto/SteveStone

Figure C11.8 ▶ Make sure you keep an accurate record of what you do as you do it.

Record keeping – your logbook

You will need to keep a record of what you do during your investigation. You do this is in a logbook. Even if you are using data loggers to collect your results and doing your analysis electronically, you should still keep a hardcopy logbook.

Scientists keep a logbook for each project that they work on. It is a record of what they did, why they did it, and what they found out. A logbook is a legal document for a working scientist. If someone's work is questioned, then the logbook acts as important evidence. Every entry in a scientist's logbook is dated, records are kept in indelible form (pen, *not pencil*), and entries may even be signed. Scientists' logbooks include details of experiments, such as methods and results. They include comments and ideas, thoughts about the experiments and analysis. They frequently include printouts of data, photocopies of relevant information, photos and other items. The logbook is the primary source of information when a scientist writes up their work for publication. Sometimes, logbooks are even provided as evidence in court cases; for example, in patent disputes or when a researcher is accused of falsifying data or stealing someone else's results.

Some scientists keep their research records electronically, but most experimental scientists still keep a hardcopy logbook. There are several advantages to a hardcopy logbook over an electronic one. First, electronic records are easy to change, and it is hard to track what was changed, when and by whom. Second, if you are working in a group, then it can be hard to keep track of who has the most recent version of the file(s). Third, files can be easily deleted or corrupted. It takes much more care and discipline to maintain a good electronic logbook than a good hardcopy. Remember that the purpose of a logbook is to record and maintain evidence of what you did. Electronic evidence is not as reliable as a signed hardcopy document.

You should talk to your teacher about what form of logbook records they require you to keep.

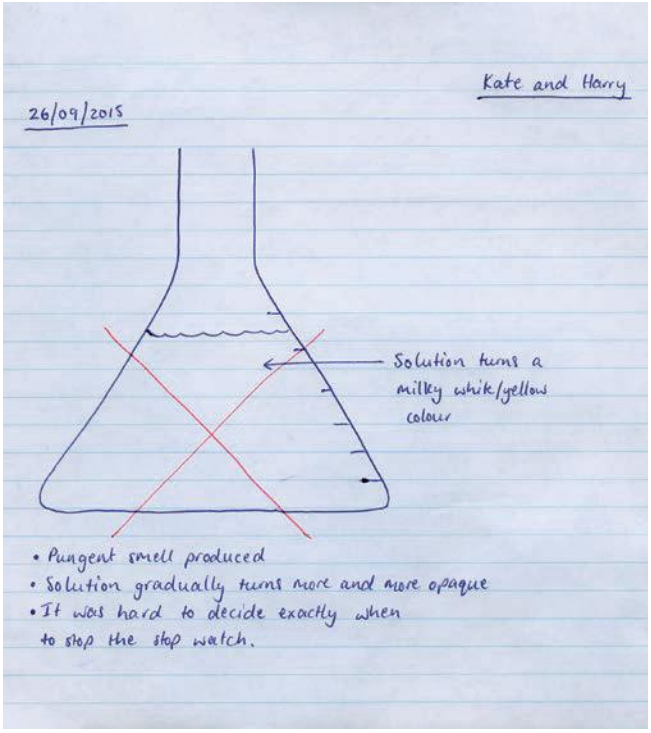
If you are working in a group, then you will need to decide whether to keep one logbook for the entire group, or one each. If you will all be working in the same places at the same times, then one for the whole group is best. If you will be in different places, such as doing field observations, then you will need one each. Your teacher may also require each of you to keep your own logbook for assessment, or for authentication purposes.

Your logbook is a detailed record of *what you did* and *what you found out* during your investigation. Make an entry in the logbook *every* time you work on your investigation. At the start of each session you should record the date and the names of all the people with whom you are working at the time.

Write down what you do as you do it. It is easy to forget what you did if you do not write it down immediately. An accurate record is important if you need to repeat any measurements or if you get unexpected results.

Write down the names, model and serial numbers of any equipment used.

Include large, clear diagrams of any experimental set-up. Label all the parts or pieces of equipment. You can also include photos of experiments. Diagrams in your logbook do not need to be neat, but you must be able to understand the diagrams later on.



◀ **Figure C11.9**
A page from a student's logbook

Record the results of *all* measurements *immediately and directly into your logbook, in pen*. *Never* record data onto bits of scrap paper instead of your logbook. Results must be recorded in indelible form. This means using a pen. Never write your results in pencil. Never use liquid paper or scribble over anything in your logbook. If you want to cross something out, just put a line through it. It is also a good idea to make a note explaining why it was crossed out.

A good logbook contains:

- **notes taken during the planning of your investigation**
- **a record of when, where and how you carried out each experiment**
- **diagrams showing the experimental set-ups, circuit diagrams, etc.**
- **all your raw results**
- **all your derived results, analysis and graphs**
- **all the ideas you had while planning, carrying out experiments and analysing data**
- **printouts, file names and locations of any data not written directly into the logbook.**

It is not a neat record, but it is a *complete* record.

Performing experiments

If you have planned carefully and learnt how to use the equipment, then your experiments should go smoothly.

As stated above, *always* record results immediately, with the correct units and with their **uncertainty**. The raw data should *always* be recorded directly into the logbook unless it is recorded using data loggers connected to a computer. In this case, a printout of the data should be attached to the logbook, and the file name and location recorded.

Make sure that you measure and record everything you will need for your analysis. This will include data such as temperature, mass or volume of chemicals, concentrations of any solutions, and any observations you make. It is much better to measure something and then discover that you didn't need to than to start your analysis and realise that you didn't measure something that you do need.

Always record the units with their uncertainty along with the measurements as you go. Do not try to add them in later.

If you are going to collect multiple data points, then it is a good idea to draw a table to record them in. Label the columns in the table with the name and units of the variables. Do not put the units in the table cells. If you know that the uncertainty in all your measurements is the same, then you can record this in the heading cell at the top of the column as well. Otherwise, each data entry should have its uncertainty recorded in the cell with it. For more explanation of recording uncertainty, see the following section.

Remember to start your analysis while you are collecting your data. As discussed in 'Planning the experimental procedure' on page 461, you will have the opportunity to repeat measurements. If you make a mistake, put a line through the mistake, write in the new data, and make a comment in your logbook. Do not scribble out or remove mistakes, they may turn out to be useful.

If you have not made a mistake, then plotting and analysing as you go allows you to spot something interesting early on. You then have a choice between revising your hypothesis or question to follow this new discovery, or continuing with your plan. Many research projects start with one question and end up answering a completely different one. These are often the most fun, because they involve something new and exciting.

Estimating uncertainties

When you perform experiments, there are typically several sources of uncertainty in your data.

Sources of uncertainty that you need to consider are the:

- **limit of reading of measuring devices**
- **precision of measuring devices**
- **variation of the measurand.**

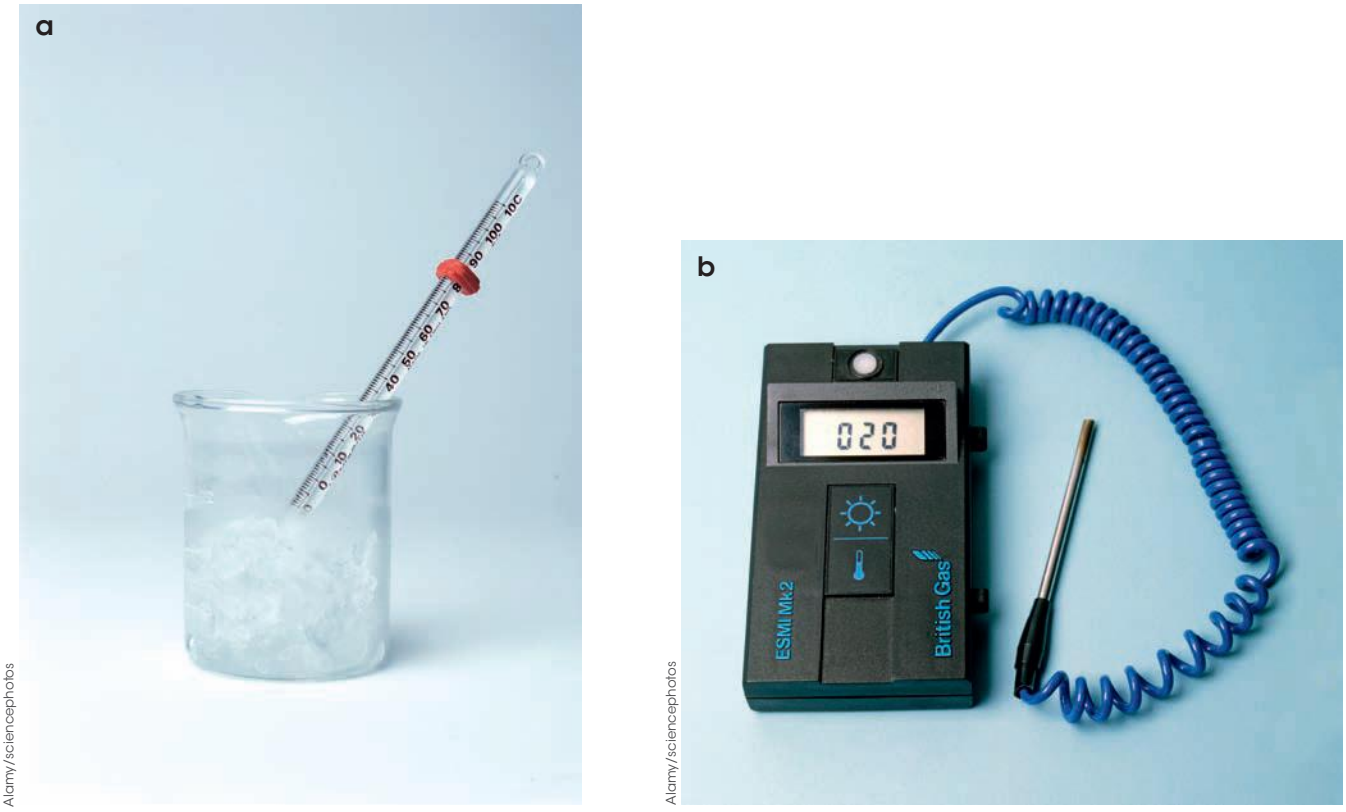
Limit of reading

For all devices there is an uncertainty due to the limit of reading of the device. The limit of reading is different for **analogue** and digital devices.

Analogue devices include swinging needle multimeters, liquid in glass thermometers and clocks with hands. Analogue devices have continuous scales. For an analogue device, the **limit of reading**, sometimes called the **resolution**, is half the smallest division on the scale. We take it as half the smallest division because you will generally be able to see which division mark that the indicator (e.g., needle, fluid level) is closest to. You may be able to estimate the measurement to one-fifth or even one-tenth of the smallest division if the spacing between divisions is large. However, the limit of reading uncertainty is still half of the smallest division. So, for a liquid in a glass thermometer with a scale marked in °C, the limit of reading is 0.5°C.

Digital devices such as digital multimeters, clocks and thermometers have a scale that gives you a number. It is limited to a specific number of figures, typically three or four, so it is a discrete scale. A digital device has a limit of reading uncertainty of a whole division. So a digital thermometer that reads to whole degrees has an uncertainty of 1°C. For a digital device, limit of reading is *always* a whole division, not a half, because you do not know whether it rounds up or down, or at what point it rounds.

The resolution or limit of reading is the *minimum* uncertainty in any measurement. Usually the uncertainty is greater than this minimum.



▲ **Figure C11.10**
a) This analogue thermometer has an uncertainty of half the smallest division on the scale.
b) This digital thermometer has an uncertainty of a degree.

Precision of measuring device

The measuring device used will have a **precision**, usually given in the user manual. For example, a multimeter may have a precision of 0.5% on a voltage scale. This means if you measure a potential difference of 12.55 V on this scale, the uncertainty due to the precision of the meter is $0.005 \times 12.55\,\text{V} = 0.06\,\text{V}$. This is greater than the limit of reading uncertainty, which is 0.01 V in this case.

Many students think that digital devices are more precise than analogue devices. This is often not the case. A digital device may be easier for you to read, but this does not mean it is more precise. The uncertainty due to the limited precision of the device is generally greater than the limit of reading.

a



Courtesy of John Morris Scientific

b

Function	Precision
pH range	0.00 to 14.00 pH
Resolution	0.01 pH
Accuracy	+/− 0.01 pH
pH slope range	80 to 120%
No. of calibration points	1 to 3 points (push-button)
Buffer options	pH 4.01, 7.00, 10.01 (USA) pH 4.01, 6.86, 9.18 (NIST) pH 4.10, 6.97 (Pb)
Temperature range	0.0 to 100.0°C
Resolution	0.1°C
Accuracy	± 0.5°C
Temperature comp.	Automatic/Manual (0 to 100°C)

Courtesy of John Morris Scientific

Figure C11.11 ▲
a) A typical pH meter.
b) A page from the user manual giving the precision on various scales

Variation of the measurand

The **measurand** (the quantity being measured) itself may vary. For example, reaction rate is strongly dependent on the temperature, concentration and other factors. Even keeping the conditions as close to identical as possible, it is unlikely that repeat experiments will give you exactly the same results. Making repeat measurements allows you to estimate the size of the variation.

Sometimes you will be able to see how the measurand varies during a measurement by watching a needle move or the readings change on a digital device. Watch and record the maximum and minimum values. The difference between these is the range:

$$\text{Range} = \text{maximum value} - \text{minimum value}$$

The value of the measurand is the average value, or the centre of the range:

$$\begin{aligned}\text{Measurand} &= \text{minimum value} + \tfrac{1}{2}(\text{range}) \\ &= \text{minimum value} + \tfrac{1}{2}(\text{maximum value} - \text{minimum value})\end{aligned}$$

The uncertainty in the measurement is half the range:

$$\text{Uncertainty} = \tfrac{1}{2}\ \text{range} = \tfrac{1}{2}(\text{maximum value} - \text{minimum value})$$

For example, if you are using an analogue multimeter and you observe that the needle fluctuates between 12.2 V and 12.6 V, then your measurement should be recorded as (12.4 ± 0.2) V. Note that the measurement and uncertainty are together in the brackets, indicating that the unit applies to both the measurement and its uncertainty.

When you take repeat measurements, the best estimate of the measurand is the average value. If you have taken fewer than 10 measurements, then the best estimate of the uncertainty is half the range. If you have more than 10 measurements, then the best estimate of the uncertainty is the standard deviation, given by:

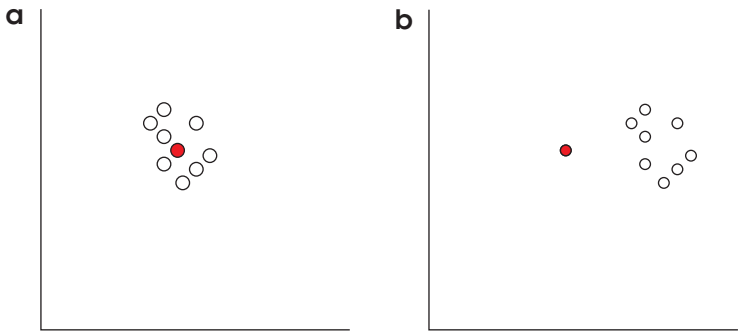
$$\text{Standard deviation} = \left(\frac{\sum (x_i - x)^2}{n-1}\right)^{\frac{1}{2}}$$

where x_i is an individual value of the measurand, x is the average value of the measurand and n is the total number of measurements. The sum is over all values of x_i. Most calculators have built-in statistical functions such as standard deviation. Spreadsheet software such as Microsoft Excel also calculates functions such as standard deviation. Remember that repeat measurements means repeating under the same conditions. It is not the same as collecting lots of data points under different conditions.

Random and systematic errors

Sources of uncertainty all give rise to **random errors**. That means that repeated measurements will be randomly spread about the '**true value**', and centred on that value.

You may also have **systematic errors** in your data. These typically occur when there is a calibration error, such as a zero error, in a measuring device. Always check that your equipment reads zero when you expect it to. For example, the pH meter should read 7 (at 25°C) in distilled water. You should also ensure that an electronic balance is tared to zero before weighing the mass of your chemicals. If your devices are not calibrated correctly, then all your readings will be faulty.



◀ Figure C11.12
a) Results are clustered about the true value when the errors are random. b) Results are clustered about some other value as a result of systematic errors.

11.4 Analysing your data

Once you have collected your data, you will need to analyse it. Record all your analyses in your logbook. If this is done on a computer, then record the file name and location and attach a printout of the analyses into your book. Many scientists have logbooks that are bulging with printouts.

The first step is organising your data. This will usually involve tabulating it. You can then graph these data. Plotting graphs is a useful way to begin the analysis of your data. Graphs are a very useful way of representing data so that you can identify trends and relationships. There are many different sorts of graphs that can be used to organise and display data. These are described on page 474.

You will usually need to do some calculations with your data to be able to answer your question or test your hypothesis. Remember to keep units on all quantities, so that any derived values have the correct units. You will also need to calculate uncertainties on any derived quantities.

GUM

Read more about uncertainties in the GUM (Guide to expressions of Uncertainty in Measurement).

Organising your data

If you have more than a few data points, then it is a good idea to display them in a table. It is important that you record all of your data in a logical manner. Clearly label each set of data so that you will know what each is when you come to analyse your data. If you have multiple experiments, then you may need a table for each. For example, if you are investigating the effect of temperature and concentration on the rate of a reaction, then you may have a table for each temperature that you tested. Each table would show the rate of the reaction for the different concentrations.

Identifying trends, patterns and relationships

You may be able to see a pattern simply by looking at a list of numbers in a table. However, the most reliable way to identify a pattern in data or a relationship between variables is to plot a graph. If you have a hypothesised equation, then use it to generate a fit on a graph of your data, as described on page 474. Do not substitute your data into your hypothesised equation and try to show that it fits.

A graph should be large and clear. The axes should be labelled with the names of the variables and their units. Choose a scale so that your data take up most of the plot area. This will often mean that the origin is not shown in your graph. Usually there is no reason why it should be.

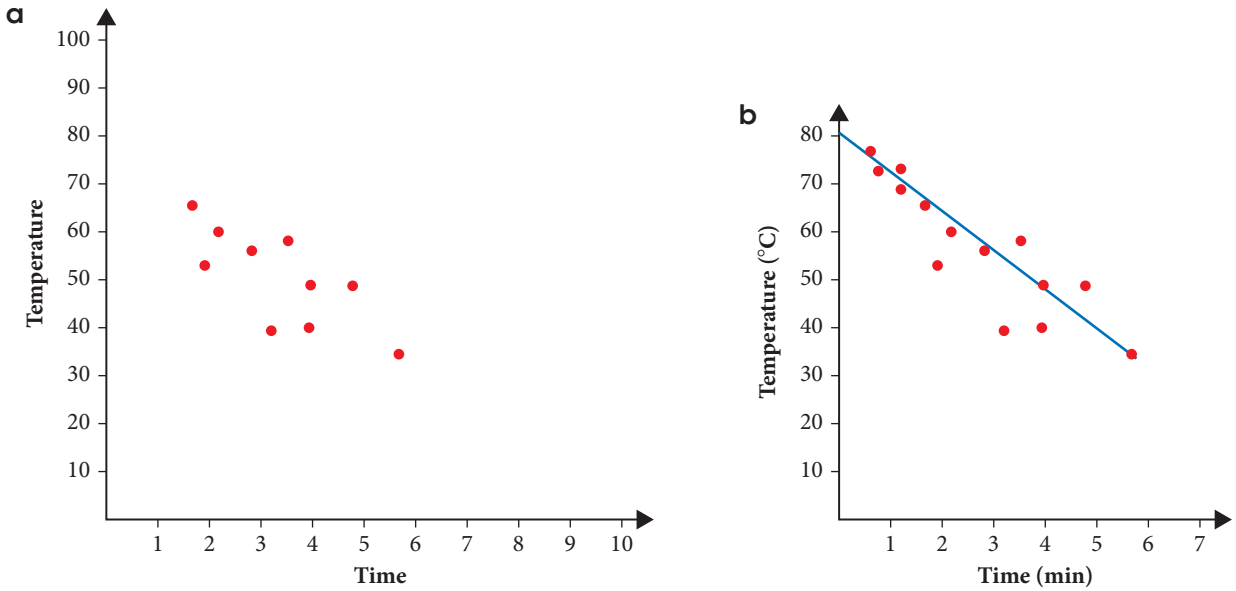


Figure C11.13 ▲
Examples of a) a poor graph and b) a good graph. How many differences can you see?

When you are looking for a relationship between variables, plot a **scatter graph**. This is a graph showing your data as points. *Do not join them up as in a dot-to-dot picture.* Usually the independent variable is plotted on the *x* axis and the dependent variable is plotted on the *y* axis, unless there is a good reason to do otherwise. In the reaction rate example, temperature would be on the *x* axis and time would be on the *y* axis.

To determine a relationship, you need to have enough data points and the range of your data points should be as large as possible. A minimum of six data points is generally considered adequate if the relationship is expected to be linear, but always collect as many as you reasonably can, given the available time.

For non-linear relationships, you need more data points than this. Try to collect more data in regions where you expect rapid variation. For example, if you are measuring the pressure of a fixed mass of gas at different volumes as shown in Figure C11.14, then you should expect an inverse relationship and therefore a hyperbola graph. If there are only a limited number of data points, it would be easy to predict the relationship to be linear instead.

DATA POINTS

Some helpful advice on deciding the number of data points.

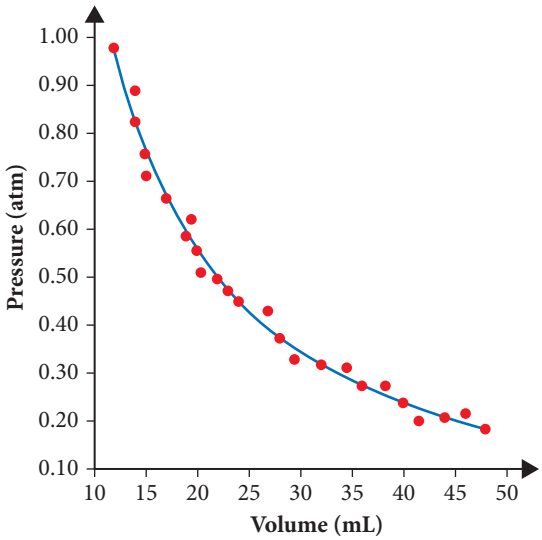


Figure C11.14 ▶
A pressure–volume graph for a gas needs a large number of data points to show the hyperbola shape.

A good graph to start with is simply a graph of the raw data. You will usually be able to tell by looking whether the graph is linear. If it is, then fit a straight line using a graphing package. You can then use a linear regression tool to check how good the straight line fit is. This will give you an R^2 number, which is a measure of 'goodness of fit'. The closer R^2 is to one (or –1), the better the fit. If it is not *very* close to one, then the relationship is not linear. Alternatively, you can calculate the uncertainty in the gradient by using lines of maximum and minimum gradient. If the uncertainty is large, then the relationship may not be linear.

If it is a linear relationship, then finding the equation for the line of best fit may be useful. *Never* force a line of best fit through the origin. Often the intercept gives you useful information. It may even indicate a systematic error, such as a zero error in the calibration of your equipment.

When you plot your raw data you may find that one or two points are outliers. These are points that do not fit the pattern of the rest of the data. These points may be mistakes; for example, they may have been incorrectly recorded or a mistake was made during measurement. They may also be telling you something important. For example, if they occur at extreme values of the independent variable, then it might be that the behaviour of the system is linear in a certain range only. You may choose to ignore outliers when fitting a line to your data, but you should be able to justify why.

When you extend a line of best fit beyond your measured points, this is called **extrapolation**. Any data that you read off a graph outside the range of your data points are extrapolated, and should be viewed with caution. You cannot say for sure that the system continues to behave in the same way beyond the bounds of your data. For example, in an investigation about the effect of enzymes on the rate of reaction at different temperatures, you may find that the rate of the reaction increases for the temperatures that you used. However, if the temperature continues to increase, then reaction rate may decrease.

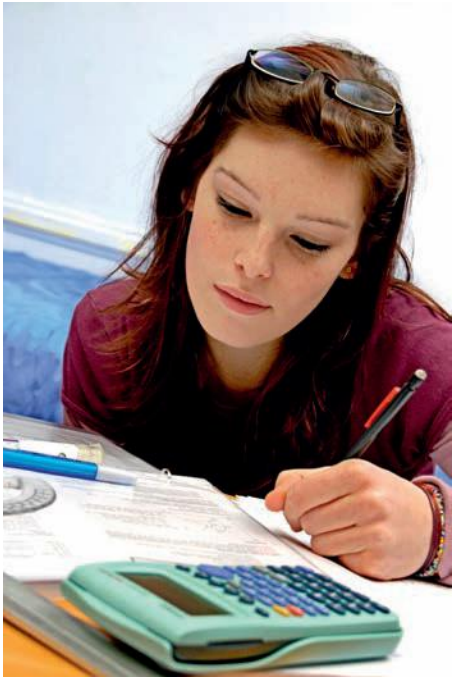
Reading points, other than data points, from a line of best fit within the region in which you have data is called **interpolation**. You cannot be sure that this is exactly what you would find if you measured that point. However, if your line of best fit really represents the behaviour of the system, then you can use interpolated points in your analysis.

Relationships between variables are often not linear. If you plot your raw data, for instance the volume and pressure of a gas, and it is a curve, *do not draw a straight line through it*. In this case, you need to think a little harder. If your hypothesis predicts the shape of the curve, then try fitting a theoretical curve to your data. If it fits well, then your hypothesis is supported.

If possible, you should **linearise** your data based on your hypothesis. Remember that linear graphs have equations of the form $y = mx + c$. Here y is the variable plotted on the vertical axis, usually the dependent variable. The independent variable x is the variable plotted on the horizontal axis. The gradient is $m = \Delta y/\Delta x$. The constant c is the y intercept.

Sometimes the relationship between variables will be more complicated than a linear relationship. In this case, a graph is still useful but the most you might be able to say is that one variable increases with another, or that there is a peak at a particular position. A graph is still a useful way of identifying trends and patterns, even if you are not able to extract a mathematical relationship from the graph.

▼ **Figure C11.15** You will usually need to analyse your raw data in some way.



Library/AJ Photo

Performing calculations with your data

You will usually have to do some calculations with your data as part of your analysis. When you recorded your data, you wrote down the units for all your measurements as well as the uncertainties. You may need to convert the units and the uncertainties to SI units; for example, mL to L. Include the units with all numbers as you do your calculations. In this way, you will make sure you have the correct units on all derived data.

It is good practice *in general*, not just in investigations, to include units at each step in all your calculations.

Interpreting your results

Once you have analysed your results, you need to interpret them. This means being able to either answer your research question or state whether your results support your hypothesis.

If your hypothesis is not supported

It is not enough to simply say 'our hypothesis is wrong'. If the hypothesis is wrong, *what* is wrong with it?

Go through your method, results and analysis. Check that your equipment was correctly calibrated, and that you were using it correctly. Check that data are recorded in the correct units, and that units are correctly carried through all calculations during analysis. Check your analysis carefully. If you are working in a group, get another person to repeat the calculations.

You should also consider what other factors may have affected your results. Were there variables that you weren't able to control? Were there variables that you forgot to control?

It is never good enough to conclude that 'the experiment didn't work'. Either a mistake was made or the model used was not appropriate for the situation. It is your job to work out which.

11.5 Communicating your results

If research is not reported on, then no one else can learn from it. An investigation is not complete until the results have been communicated. Most commonly a report is written.

Writing reports

A report is a formal and carefully structured account of your research. It is based on the data and analysis in your logbook. However, the report is a *summary*. It contains only a small fraction of what appears in the logbook. Your logbook contains all your ideas, rough working and raw data. The report typically contains none of this.

A report consists of several distinct sections, each with a particular purpose. These are:

- Abstract
- Introduction
- Materials
- Method
- Results and analysis
- Discussion
- Conclusion
- Acknowledgements
- References
- Appendices

Reports are always written in the third person and past tense, because they describe what you have done.

Abstract

The abstract is a very short summary of the entire report. It is the most important part, because often it is the only part that people read. Typically an abstract is between 50 and 200 words long. It appears at the start of the report, but is always the last section that you write. Try writing just one sentence to summarise each part of your report.

Introduction

The introduction tells the reader why you did the investigation and what your research question or hypothesis is. This is the place to explain why this research is interesting.

The introduction also provides any background information needed to be able to understand the rest of the report. This is the place to summarise any existing theories and models. You need to do this to justify your hypothesis. You should also summarise any similar investigations. All of this should be correctly referenced, as described in the References section on page 475.

Method

The method describes what you did. It is not a recipe for someone else to follow.

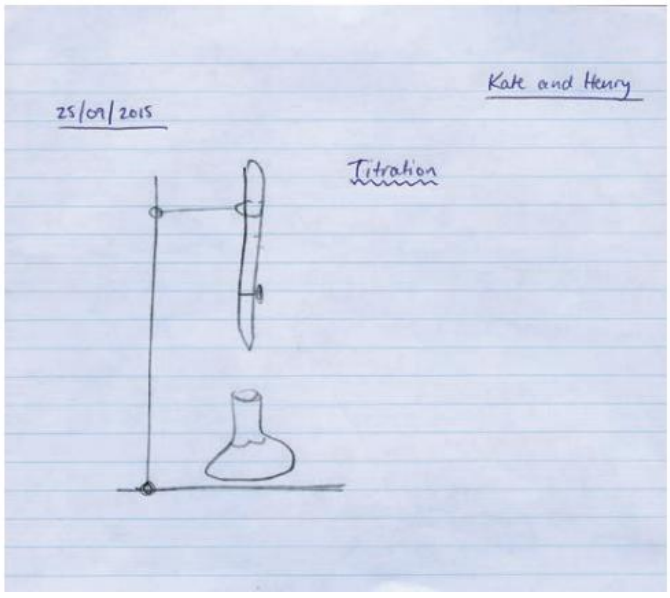
The method summarises what you measured and how you measured it. It also explains, briefly, why you chose a particular method or technique.

Write your method using sentences, not dot points. Remember that these need to be written in past tense – *it is not a recipe*. You are not commanding anyone to do anything. You are telling people what you did. For example, you would write 'The temperature was measured', not 'Record the temperature'.

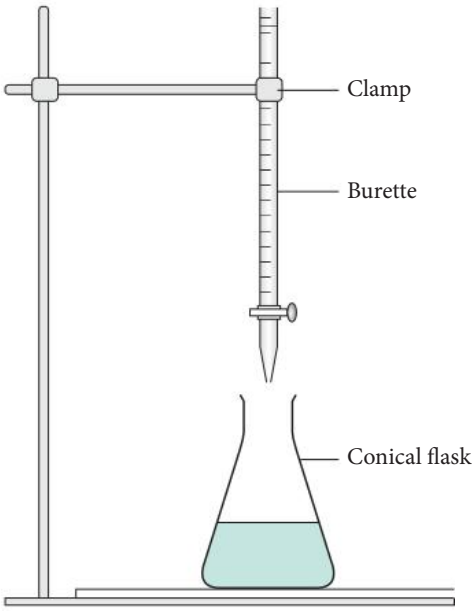
Include any diagrams needed to make your method clear. The diagrams in your logbook will usually be rough sketches (see Figure C11.16). The figures in your report should be very neat and carefully labelled. Flowcharts can be useful to describe any procedures in which a series of steps was followed. Each included item should have a number and you should refer to it in the text of your report. Position each item close to where it is referred to in the text. You should take the time to learn how to position figures neatly using your word processor software.

▼ **Figure C11.16**
a) A sketch of a titration from a logbook and b) a scientific illustration for a report

a



b



Results and analysis

The results section is a *summary* of your results. It is usually combined with the analysis section, although they may be kept separate.

Avoid including tables of raw data in your report unless they compare the results of a few different experiments. For example, you would include a table showing time taken for the reaction at different temperatures.

If a table has more than a few rows of data, it is better to represent those data in some other way. Usually this will be a graph.

Where appropriate, you should also include a graph to represent your data. However, your graph should be for the averages, not all the raw data. Think about what sort of graph is appropriate. If you want to show a relationship between two variables, then use a scatter plot. Display your data as points and clearly label any lines you have fitted to the data. Always make sure you label your axes, including units. Choose an appropriate scale so that the data take up most of the plot area.

Column and bar charts are useful for comparing two data sets, such as the average time taken for 5 grams of calcium carbonate chips and powder to react. *Do not* use a column or bar chart to try to show a mathematical relationship between variables. Remember to add headings for all figures and tables.

Figure C11.17 gives examples of the two types of graphs.

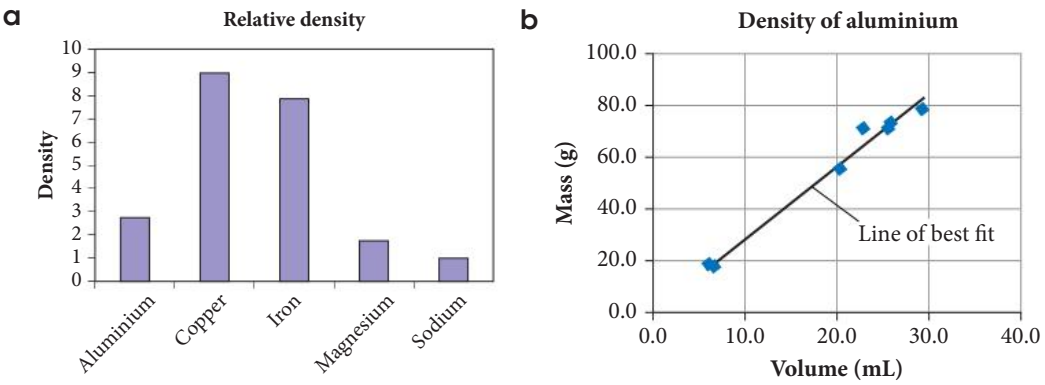


Figure C11.17 ▶
a) A column graph can be used for discrete data. b) A line graph or a scatter plot is used to show a mathematical relationship between continuous data.

Any data and derived results should be given in correct SI units with their uncertainties. If you performed calculations, then show the equations you used. You might want to show one example of your calculation, but do not show more than one if the procedure used is repeated.

Discussion

The discussion should summarise *what your results mean*. If you began with a research question, then give the answer to the question here. If you began with a hypothesis, then state whether your results support your hypothesis or not. If not, explain why. You may not be able to say why, other than that the model was not suitable for the situation being investigated.

If there are any implications of your work, such as what conditions to use for a reaction or which materials to use for a particular purpose, then put them here.

The discussion is also the place to briefly describe any difficulties that you had and make suggestions for improving the process. Remember that you should never say 'the experiment didn't work' if you didn't get the results you expected. You might choose to make some comments on a more appropriate model and possible further work that could be done.

Conclusion

The conclusion is a *very* brief summary of the results and their implications. Say what you found out and what it means. A conclusion should only be a few sentences long.

Acknowledgements

You should thank anyone who helped you in your investigation. This includes people who supplied equipment or funding, as well as people who gave you good ideas or helped with the analysis. In science, as in other aspects of your life, it is polite to say thank you; however, this is not a necessary section of a report.

REFERENCING GUIDE

This guide is designed to help you with referencing your sources for assignments.

References

A reference list details the source of each piece of information used, and is linked to that information in the report.

A reference list details the sources of all information that was used to write the report. Wherever a piece of information or quotation is used in your report, it must be referenced *at that point*. This is typically done by placing either a number in brackets at the point [2], or the author and year of publication (Smith, 2014). The reference list is then provided either in a footnote at the end of the page, or as a single complete list at the end of the report. Referencing must be done in a consistent style. Check with your teacher what style they prefer. There are several good online guides to referencing.

A reference list is *not* the same as a bibliography. A bibliography is a list of sources that are useful to understanding the research. They may or may not have been used by the report authors. You should have a bibliography in your logbook from the planning stage of your investigation. The references will be a subset of these sources.

Appendices

Appendices may be used to provide additional information such as raw data that is not necessary to understanding the report but which might be of interest to some readers. Your teacher might require you to provide raw data in an appendix. Reports do not always have appendices.

Other ways of communicating your results

You may want to present the results of your investigation in another way. Scientists communicate their work in many ways; for example, by presenting a poster or seminar. They may write an article or produce a website. Scientists usually use more than one way, and sometimes several, to communicate about a really interesting investigation.

Look at examples of articles in the scientific and popular media, on websites, posters and so on. This will give you an idea of the different styles used in the different modes. Think about the purpose. Is it to inform, to persuade or both? What sort of language is used?

Think about your audience and use appropriate language and style. A poster is not usually as formal as a report. A website may be more or less formal, depending on your audience.

Posters and websites use a lot of images. Images are usually more appealing than words and numbers, but they need to be relevant. Make sure they communicate the information you want them to.

Keep readability and accessibility in mind if you are creating a poster or website. Posters should use large clear fonts and not have too much text. They should be readable from a few metres away.



Reproduced with permission of Helen Kiriazis (photographer) and Heart News & Views. International Society for Heart Research

Figure C11.18 A poster session is a common way to present scientific findings at a conference.

REFERENCING I-TUTORIAL

This tutorial will help you understand referencing and show you how to avoid plagiarism.

REPORT WRITING EXAMPLE 1

The brochure outlines the key features of a design report.

REPORT WRITING EXAMPLE 2

This online resource guides you through the sections of a typical report.

REPORT WRITING EXAMPLE 3

This online resource will help you write a case study.

WEBSITE ACCESSIBILITY

The Royal Society for the Blind has information on making websites accessible.

Fonts also need to be large enough and clear on websites and digital images should have tags. Follow the weblink 'Website accessibility' for more information on accessibility and web-page design.

However you communicate your work, make sure you know what the message is and who the audience is. Once you have established that, you will be able to let other people know about the interesting things you have discovered in your investigation.

CHAPTER GLOSSARY

analogue a device or scale that gives a continuous measurement; the scale is continuous and may show any value in a range

continuous able to include any value, sometimes within a fixed range; for example, a rainbow is a continuous spectrum

dependent variable the variable that changes as a result of changes to the independent variable

discrete able to include only specific values, not continuous; for example, a line spectrum is a discrete spectrum

extrapolation extension beyond the measured range of data to read or construct new data that have not been measured

falsifiable able to be disproved

hypothesis a tentative prediction, usually based on an existing model or theory. Also a tentative explanation of an observation based on an existing model or theory

independent variable a variable upon which another variable depends

interpolation to read or construct a new data point that has not been measured but is within the range of measured data

limit of reading the minimum uncertainty in a measurement due to the precision with which the scale can be read

line of best fit the line that most accurately fits the data, usually calculated using linear regression

linearise to make linear; to convert into a form that can be described by a straight line

logbook the record of an experiment or investigation kept by the scientist performing the experiments; it is a legal record of the experiments and their results

measurand the quantity being measured

model a representation of a system or phenomena that explains the system or phenomena. A model may be mathematical equations, a computer simulation, a physical object, words or other form

outlier a data point that does not fit the pattern shown by other measured data points

plagiarism presenting someone else's work, including their words or ideas, as your own

precision the variation in repeated measurements, or the uncertainty of a measuring device

primary data data that you have measured or collected yourself

qualitative measurement a measurement with descriptive or non-numerical results

quantitative measurement a measurement with a numerical value

random error a variation that affects a measurement in a random way so that the measurement is as likely to change in any one direction as in any other

reference the source of a specific piece of information or quotation

reliable highly likely to be true; a trustworthy source of information or reproducible data

reproducible giving the same result, within uncertainty, when repeated measurements are made

research question the specific question that a particular experiment or investigation is attempting to answer

resolution the limit of reading or precision of a measuring device

scatter graph a graph or plot showing data points, without a line joining the points, and used to demonstrate or determine a mathematic relationship between variables. The axes are defined by the variables

secondary data data or information that has been collected by someone else

systematic error an error that acts to give a consistent offset in data; for example, a zero error

theory a collection of models and concepts that explain specific systems or phenomena. Scientific theories allow predictions to be made and hence are falsifiable

true value the exact value of a measurand; an idealisation as all measurements have uncertainty and many measurands have values that vary

uncertainty an estimate of the range of values within which the 'true value' of a measurement or derived quantity lies

valid results that are affected only by a single independent variable and hence are reproducible

variable something that can change or be changed, as distinct from a constant, which does not

APPENDICES

Appendix 1: Periodic table

Appendix 2: Relative atomic masses (atomic weights) of common elements

Element	Symbol	Relative atomic mass	Element	Symbol	Relative atomic mass
Aluminium	Al	26.98	Lead	Pb	207.2
Antimony	Sb	121.75	Lithium	Li	6.94
Argon	Ar	39.95	Magnesium	Mg	24.31
Arsenic	As	74.92	Manganese	Mn	54.94
Barium	Ba	137.34	Mercury	Hg	200.59
Beryllium	Be	9.01	Molybdenum	Mo	95.94
Bismuth	Bi	208.98	Neon	Ne	20.18
Boron	B	10.81	Nickel	Ni	58.71
Bromine	Br	79.90	Niobium	Nb	92.91
Cadmium	Cd	112.41	Nitrogen	N	14.01
Caesium	Cs	132.91	Osmium	Os	190.2
Calcium	Ca	40.08	Oxygen	O	16.00
Carbon	C	12.01	Palladium	Pd	106.4
Cerium	Ce	140.12	Phosphorus	P	30.97
Chlorine	Cl	35.45	Platinum	Pt	195.09
Chromium	Cr	52.00	Potassium	K	39.10
Cobalt	Co	58.93	Radium	Ra	226.03
Copper	Cu	63.55	Rhenium	Re	186.2
Fluorine	F	19.00	Rhodium	Rh	102.91
Gallium	Ga	69.72	Rubidium	Rb	85.47
Germanium	Ge	72.59	Ruthenium	Ru	101.07
Gold	Au	196.97	Scandium	Sc	44.96
Hafnium	Hf	178.49	Selenium	Se	78.96
Helium	He	4.00	Silicon	Si	28.09
Hydrogen	H	1.01	Silver	Ag	107.87
Indium	In	114.82	Sodium	Na	22.99
Iodine	I	126.90	Strontium	Sr	87.62
Iridium	Ir	192.22	Sulfur	S	32.06
Iron	Fe	55.85	Tantalum	Ta	180.95
Krypton	Kr	83.80	Technetium	Tc	98.91
Lanthanum	La	138.91	Tellurium	Te	127.60

Element	Symbol	Relative atomic mass	Element	Symbol	Relative atomic mass
Thallium	Tl	204.37	Vanadium	V	50.94
Thorium	Th	232.04	Xenon	Xe	131.30
Tin	Sn	118.69	Yttrium	Y	88.91
Titanium	Ti	47.90	Zinc	Zn	65.38
Tungsten	W	183.85	Zirconium	Zr	91.22
Uranium	U	238.03			

Appendix 3: Guidelines for using significant figures

When we measure quantities on instruments, the last figure in the measurement is usually uncertain. This is because of the in-built uncertainty in the instrument itself, even if we have avoided errors such as parallax error. Thus, if our electronic balance gives a reading of, say, 10.514 g, then we need to be aware that the last figure (4) will be uncertain. It is likely that the true mass is somewhere between 10.512 g and 10.516 g.

Significant figures show how many digits in the reading are meaningful. The last figure is always deemed to be uncertain. By keeping track of the number of significant figures in all the instrumental measurements used to calculate a quantity, we can determine the extent to which our answer correctly represents the accuracy of our instruments. To reflect this accuracy, we always give our answer to the same number of significant figures as the *least accurate* data used. (If we use an even lower number of significant figures than this, then we might as well use less accurate instruments!)

The rules

1 Every non-zero digit is significant. For example, 3.78 and 294 both have 3 significant figures.

2 Every zero in the middle of a reading is significant. For example, the mass reading of 10.514 g has 5 significant figures.

3 Every zero to the right of a reading is significant. For example, 31.20 has 4 significant figures. The exception to this is a number with no decimal point and a trail of zeros, such as 500 mL. This volume may have 1, 2 or 3 significant figures. To avoid this ambiguity, we must be given more information, stated in standard form. For example, if the volume is provided as 5.00×10^2 mL, then we know that it has 3 significant figures. If this is not clarified, we assume that it has the maximum number of significant figures.

4 Every zero before a number is not significant, and only shows the place value. For example, 0.005 only has 1 significant figure and 0.0090 has 2 significant figures. Again, rewriting these numbers in standard form clarifies this. (These numbers would be written as 5×10^{-3} and 9.0×10^{-3} respectively.)

Calculations

Rounding off

For rounding off an answer to a given number of significant figures, we examine the next figure on the right only. If it is 5 or more, then we round up.

Example

If we need to round off 10.9847 to:

- 4 significant figures, then we write 10.98 (8 is the fourth significant figure. The next figure on the right of 8 is 4, so we do not round up.)
- 3 significant figures, then we write 11.0. (9 is the third significant figure. The next figure on the right of 9 is 8, so we round up. Adding 1 to the 9 causes 10.9 to become 11.0.)

Adding or subtracting numbers

The answer cannot have more significant figures after the decimal point (i.e. decimal places) than the least accurate data.

Example

73.251 ← 3 decimal places

+1.4 ← 1 decimal place; therefore, this is the least accurate data

74.651

This answer cannot have more than 1 decimal place, so must be rounded off to 74.7.

Multiplying or dividing numbers

Again, the answer cannot have more significant figures than the least accurate data.

Example

$7.53 \times 6.0958 = 45.9$ (to 3 significant figures)

The least accurate figure (7.53) has 3 significant figures, so we round off the answer to 3 significant figures.

Use of data such as relative atomic masses

Ideally, physical data such as relative atomic masses and molar volumes should be quoted to at least the same number of significant figures as the experimental data.

However, physical data is not taken into account when determining the number of significant figures in the answer – only experimental data such as masses and volumes is considered.

Advice

Data provided in a question or in a test should not be rounded off prior to its use in a calculation. For example, if A_r(H) is given as 1.0 amu, then in a calculation we write 1.0, not 1. Similarly, if a volume is given as 20.00 mL, we write 20.00 in the calculation, not 20 (even though on our calculator we would only enter the number as 20). This makes the accuracy of the reading clear for the purposes of determining the number of significant figures we provide in the answer.

Appendix 4: Common ions, ion colours, flame colours and solubilities

Polyatomic ions

1+	1–	2–	3–
Ammonium NH_4^+	Nitrate NO_3^-	Carbonate CO_3^{2-}	Phosphate PO_4^{3-}
Hydronium H_3O^+	Nitrite NO_2^-	Sulfate SO_4^{2-}	
	Hydrogen carbonate HCO_3^-	Sulfite SO_3^{2-}	
	Hydrogen sulfate HSO_4^-	Hydrogen phosphate HPO_4^{2-}	
	Dihydrogen phosphate $H_2PO_4^-$	Dichromate $Cr_2O_7^{2-}$	
	Hydroxide OH^-	Silicate SiO_3^{2-}	
	Permanganate MnO_4^-		
	Thiocyanate SCN^-		
	Hypochlorite OCl^-		
	Ethanoate (acetate) CH_3COO^-		

Ion colours and flame colours

Ion	Solution colour	Ion	Flame colour
Groups 1, 2, 17	Colourless	Li^+	Bright red
Cr^{2+}	Blue	Na^+	Yellow
Cr^{3+}	Green	K^+	Violet
Co^{2+}	Pink	Ca^{21}	Yellow-red
Cu^+	Green	Sr^{2+}	Bright red
Cu^{2+}	Blue	Ba^{2+}	Yellow-green
Fe^{2+}	Pale green	Cu^{2+}	Blue (halides); green (others)
Fe^{3+}	Yellow–brown	Pb^{2+}	Light blue-grey
Mn^{2+}	Pale pink	Zn^{2+}	Whitish green
Ni^{2+}	Green		
$Cr_2O_7^{2-}$	Orange		
MnO_4^-	Purple		

Solubility of ionic compounds at standard laboratory conditions (SLC)

Anion	Cl^-, Br^-, I^-	S^{2-}	OH^-	SO_4^{2-}	CO_3^{2-}, PO_4^{3-}, SO_3^{2-}	CH_3COO^-	NO_3^-
High solubility (aq) $\geq$ 0.1 mol L^{-1} (at SLC)	Most	Group 1, group 2 NH_4^+	Group 1, Sr^{2+}, Ba^{2+}, NH_4^+	Most	Group 1, NH_4^+	Most	All
Low solubility (s) $<$ 0.1 mol L^{-1} (at SLC)	Ag^+, Pb^{2+}, Cu^+	Most	Most	Ag^+, Pb^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}	Most	Ag^+	None

All group 1 compounds and all ammonium compounds have high solubility in water.

Appendix 5: Common units of measurement

Common values of mass, temperature and pressure

1 tonne (1 t) = 10^6 g = 1 Mg

STP = 0°C and 100 kPa

SLC = 25°C and 100 kPa

0°C = 273.15 K

1 atm = 101.325 kPa = 760 mmHg

Standard values

Avogadro constant
$N_A = 6.022 \times 10^{23}$ particles mol^{-1}

Universal gas constant R = 8.31 kPa L mol^{-1} K^{-1}

Molar volume of gases V_M = 22.711 L mol^{-1} at STP; 24.790 L mol^{-1} at SLC

Density of water = 1.00 g cm^{-3} at 25°C

Prefixes for physical quantities

Fraction	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-1} (tenth)	deci	d	10^1 (ten)	deca	da
10^{-2} (hundredth)	centi	c	10^2 (hundred)	hecto	h
10^{-3} (thousandth)	milli	m	10^3 (thousand)	kilo	k
10^{-6} (millionth)	micro	μ	10^6 (million)	mega	M
10^{-9} (billionth)	nano	n	10^9 (billion)	giga	G

Appendix 6 Acid–base indicators

Common name of indicator	Colour of HIn(aq)	Approximate pH range	Colour of In^-(aq)
Methyl violet	Yellow	0.0–1.6	Blue
Thymol blue	Red	1.2–2.8	Yellow
Orange IV	Red	1.4–2.8	Yellow
Benzopurpurine-48	Violet	2.2–4.2	Red
Congo red	Blue	3.0–5.0	Red
Methyl orange	Red	3.2–4.4	Yellow
Bromocresol green	Yellow	3.8–5.4	Blue
Methyl red	Red	4.8–6.0	Yellow
Chlorophenol red	Yellow	5.2–6.8	Red
Bromothymol blue	Yellow	6.0–7.6	Blue
Litmus	Red	6.0–8.0	Blue
Phenol red	Yellow	6.6–8.0	Red
Metacresol purple	Yellow	7.4–9.0	Purple
Thymol blue	Yellow	8.0–9.6	Blue
Phenolphthalein	Colourless	8.2–10.0	Red
Thymolphthalein	Colourless	9.4–10.6	Blue
Alizarin yellow R	Yellow	10.1–12.0	Red
Indigo carmine	Blue	11.4–13.0	Yellow
1,3,5-trinitrobenzene	Colourless	12.0–14.0	Orange

Appendix 7 Relative acid strengths

Per cent reaction with water	Acid		Conjugate base	
	Name	Formula	Name	Formula
100	Perchloric acid	$HClO_4$(aq)	Perchlorate ion	ClO_4^-(aq)
100	Hydroiodic acid	HI(aq)	Iodide ion	I^-(aq)
100	Hydrobromic acid	HBr(aq)	Bromide ion	Br^-(aq)
100	Hydrochloric acid	HCl(aq)	Chloride ion	Cl^-(aq)
100	Sulfuric acid	H_2SO_4(aq)	Hydrogen sulfate ion	HSO_4^- (aq)
100	Nitric acid	HNO_3(aq)	Nitrate ion	NO_3^-(aq)
–	Hydronium ion	H_3O^+(aq)	Water	H_2O(l)
51	Oxalic acid	HOOCCOOH(aq)	Hydrogen oxalate ion	$HOOCCOO^-$(aq)

30	Sulfurous acid	$(SO_2 + H_2O)$ $H_2SO_3(aq)$	Hydrogen sulfite ion	$HSO_3^-(aq)$
27	Hydrogen sulfate ion	$HSO_4^-(aq)$	Sulfate ion	$SO_4^{2-}(aq)$
23	Phosphoric acid	$H_3PO_4(aq)$	Dihydrogen phosphate ion	$H_2PO_4^-(aq)$
8.2	Citric acid	$H_3C_6H_5O_7(aq)$	Dihydrogen citrate ion	$H_2C_6H_5O_7^-(aq)$
8.1	Nitrous acid	$HNO_2(aq)$	Nitrite ion	$NO_2^-(aq)$
7.8	Hydrofluoric acid	HF(aq)	Fluoride ion	$F^-(aq)$
4.2	Methanoic (formic) acid	HCOOH(aq)	Methanoate ion	$HCOO^-(aq)$
1.3	Ethanoic (acetic) acid	$CH_3COOH(aq)$	Ethanoate (acetate) ion	$CH_3COO^-(aq)$
–	Carbonic acid	$(CO_2 + H_2O)$ $H_2CO_3(aq)$	Hydrogen carbonate ion	$HCO_3^-(aq)$
0.10	Hydrosulfuric acid	$H_2S(aq)$	Hydrogen sulfide ion	$HS^-(aq)$
0.079	Dihydrogen phosphate ion	$H_2PO_4^-(aq)$	Hydrogen phosphate ion	$HPO_4^{2-}(aq)$
0.079	Hydrogen sulfite ion	$HSO_3^-(aq)$	Sulfite ion	$SO_3^{2-}(aq)$
0.054	Hypochlorous acid	HClO(aq)	Hypochlorite ion	$ClO^-(aq)$
0.0078	Hydrocyanic acid	HCN(aq)	Cyanide ion	$CN^-(aq)$
0.0076	Ammonium ion	$NH_4^+(aq)$	Ammonia	$NH_3(aq)$
0.0022	Hydrogen carbonate ion	$HCO_3^-(aq)$	Carbonate ion	$CO_3^{2-}(aq)$
0.00020	Hydrogen phosphate ion	$HPO_4^{2-}(aq)$	Phosphate ion	$PO_4^{3-}(aq)$
0.00011	Hydrogen sulfide ion	$HS^-(aq)$	Sulfide ion	$S^{2-}(aq)$
–	Water	$H_2O(l)$	Hydroxide ion	$OH^-(aq)$

- The per cent reaction of acids with water is for 0.10 mol L^{-1} solutions and is only valid for concentrations close to 0.10 mol L^{-1}. All measurements of acid strengths were made under standard laboratory conditions (SLC).
- No per cent reaction is given for carbonic acid because this acid has a molar solubility of less than 0.10 mol L^{-1} at SLC.
- Values in this table for 25°C are taken from Dean, J. A. (Ed) (1991). *Lange's Handbook of Chemistry*, 15th edition, McGraw-Hill.

Appendix 8 Standard electrode potentials at 25°C

	Oxidised form + ne^- → Reduced form		E° (V)	
Oxidising strength increases ↑	$F_2 + 2e^-$	$\rightarrow 2F^-$	+2.87	↓ Reducing strength increases
	$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	+1.78	
	$Au^+ + e^-$	$\rightarrow Au$	+1.69	
	$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	+1.51	
	$PbO_2 + 4H^+ + 2e^-$	$\rightarrow Pb^{2+} + 2H_2O$	+1.46	
	$Cl_2 + 2e^-$	$\rightarrow 2Cl^-$	+1.36	
	$O_3 + H_2O + 2e^-$	$\rightarrow O_2 + 2OH^-$	+1.24	
	$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	+1.23	
	$O_2 + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	+1.23	
	$MnO_2 + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	+1.22	
	$Pt^{2+} + 2e^-$	$\rightarrow Pt$	+1.18	
	$Ag_2O + 2H^+ + 2e^-$	$\rightarrow 2Ag + H_2O$	+1.17	
	$Br_2 + 2e^-$	$\rightarrow 2Br^-$	+1.09	
	$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO + 2H_2O$	+0.96	
	$NO_3^- + 3H^+ + 2e^-$	$\rightarrow HNO_2 + H_2O$	+0.93	
	$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	+0.92	
	$Hg^{2+} + 2e^-$	$\rightarrow Hg$	+0.85	
	$NO_3^- + 2H^+ + e^-$	$\rightarrow NO_2 + H_2O$	+0.80	
	$Ag^+ + e^-$	$\rightarrow Ag$	+0.80	
	$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	+0.77	
	$O_2 + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	+0.70	
	$MnO_4^- + 2H_2O + 3e^-$	$\rightarrow MnO_2 + 4OH^-$	+0.60	
	$I_2 + 2e^-$	$\rightarrow 2I^-$	+0.54	
	$O_2 + 2H_2O + 4e^-$	$\rightarrow 4OH^-$	+0.40	
	$Ag_2O + H_2O + 2e^-$	$\rightarrow 2Ag + 2OH^-$	+0.34	
	$Cu^{2+} + 2e^-$	$\rightarrow Cu$	+0.34	
	$SO_4^{2-} + 4H^+ + 2e^-$	$\rightarrow H_2SO_3 + H_2O$	+0.17	
	$Sn^{4+} + 2e^-$	$\rightarrow Sn^{2+}$	+0.15	
	$S + 2H^+ + 2e^-$	$\rightarrow H_2S$	+0.14	
	$S_4O_6^{2-} + 2e^-$	$\rightarrow 2S_2O_3^{2-}$	+0.08	
	$2H^+ + 2e^-$	$\rightarrow H_2$	0.00	
	$Pb^{2+} + 2e^-$	$\rightarrow Pb$	−0.13	
	$Sn^{2+} + 2e^-$	$\rightarrow Sn$	−0.14	
	$Ni^{2+} + 2e^-$	$\rightarrow Ni$	−0.26	
	$Co^{2+} + 2e^-$	$\rightarrow Co$	−0.28	
	$PbSO_4 + 2e^-$	$\rightarrow Pb + SO_4^{2-}$	−0.36	
	$Cd^{2+} + 2e^-$	$\rightarrow Cd$	−0.40	
	$Fe^{2+} + 2e^-$	$\rightarrow Fe$	−0.45	
	$2CO_2 + 2H^+ + 2e^-$	$\rightarrow H_2C_2O_4$	−0.49	
	$Zn^{2+} + 2e^-$	$\rightarrow Zn$	−0.76	
	$2H_2O + 2e^-$	$\rightarrow H_2 + 2OH^-$	−0.83	
	$Al^{3+} + 3e^-$	$\rightarrow Al$	−1.66	
	$Mn^{2+} + 2e^-$	$\rightarrow Mn$	−1.81	
	$Mg^{2+} + 2e^-$	$\rightarrow Mg$	−2.37	
	$Na^+ + e^-$	$\rightarrow Na$	−2.71	
	$Ca^{2+} + 2e^-$	$\rightarrow Ca$	−2.87	
	$Ba^{2+} + 2e^-$	$\rightarrow Ba$	−2.91	
	$K^+ + e^-$	$\rightarrow K$	−2.93	
	$Li^+ + e^-$	$\rightarrow Li$	−3.04	

State symbols (phase descriptors) have been omitted in order not to clutter up what is already a complex table. All ions are present as aqueous solutions; other substances are present in their stable pure forms at 25°C and 100kPa.

On the large side arrows, 'oxidising strength' refers to the oxidised form of the redox couple and 'reducing strength' refers to the reduced form of the couple.

NUMERICAL ANSWERS

Chapter 1

Question set 1.1

6 a $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$

b $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Question set 1.2

5 a $K = \dfrac{[HCl]^2}{[H_2] \times [Cl_2]}$

b $K = \dfrac{[SO_4^{2-}] \times [H_3O^+]}{[HSO_4^-]}$

7 $Q = \dfrac{[CH_3OH]}{[CO] \times [H_2]^2} = \dfrac{5}{0.5 \times (0.5)^2} = 40$

Chapter review questions

7 $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

$K = \dfrac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]}$

11 a $CuCO_3(s) \rightleftharpoons CuO(s) + CO_2(g)$

b $K = [CO_2]$

Chapter 2

Question set 2.1

3 a HNO_3 / NO_3^- ; H_2O / H_3O^+

b NH_4^+ / NH_3 ; H_2O / H_3O^+

c HSO_4^- / SO_4^{2-} ; O^{2-} / OH^-

d $H_2PO_4^-$ / HPO_4^{2-} ; CO_3^{2-} / HCO_3^-

e $HC_2H_3O_2$ / $C_2H_3O_2^-$; / HS^- / H_2S

4 a H_2CO_3

b H_2O

c $H_2PO_4^-$

Question set 2.2

3 $Kw = 10^{-14}$

4 a $[H_3O^+] = 10^{-5}$ M, $[OH^-] = 10^{-9}$ M

b $[H_3O^+] = 10^{-14} = 1$ M, $[OH^-] = 10^0$ M

c $[H_3O^+] = 10^{-3}$ M, $[OH^-] = 10^{-11}$ M

d $[H_3O^+] = 10^{-8}$ M, $[OH^-] = 10^{-6}$ M

6 a i 2

ii 12

iii 0

iv 13

v 2

vi 0.64

vii 1.76

viii −0.10

b 4.48

7 a $10^{-3} = 0.001$ M

b $[H^+] = 10^{-11.5}$ $[OH^-] = \dfrac{10^{-14}}{10^{-11.5}} = 10^{-2.5} = 0.0032$ M

c $[H^+] = 10^{-10}$ $[OH^-] = \dfrac{10^{-14}}{10^{-10}} = 10^{-4} = 0.0001$ M

$[Ca(OH)_2] = \dfrac{1}{2} \times 0.0001 = 0.00005$ M

d $10^{-3} = 0.001$ M. Sulfuric acid is diprotic, so $[H_2SO_4] = 0.0005$ M.

8 a $n(HCl) = cV = 0.2 \times 50 \times 10^{-3} = 10 \times 10^{-3} = 1 \times 10^{-2}$

$n(NaOH) = cV = 0.1 \times 100 \times 10^{-3} = 1 \times 10^{-2}$

pH = 7 because $[H^+] = [OH^-]$

b $\dfrac{10^{-6}}{2} = 5 \times 10^{-7} = 0.0000005$ M

pH = 6.3

Question set 2.3

1 a $K_a = \dfrac{[OBr^-][H_3O^+]}{[HOBr]}$

b $K_a = \dfrac{[CN^-][H_3O^+]}{[HCN]}$

c $K_a = \dfrac{[NH_3][H_3O^+]}{[NH_4^+]}$

3 a i $HS^- + HCl \rightarrow H_2S + Cl^-$

ii $HSO_3^- + HCl \rightarrow H_2SO_3 + Cl^-$

iii No reaction

iv $H_2NCH(CH_3)COOH + HCl \rightarrow H_3N^+CH(CH_3)COOH + Cl^-$

b i $HS^- + NaOH \rightarrow S^{2-} + Na^+ + H_2O$

ii $HSO3^- + NaOH \rightarrow H_2O + Na^+ + SO_3^{2-}$

iii $HCOOH + NaOH \rightarrow HCOO^- + Na^+ + H_2O$

iv $H_2NCH(CH_3)COOH + NaOH \rightarrow H_2NCH(CH_3)COO^- + Na^+ + H_2O$

5 $K_a = 1.05 \times 10^{-10} = \dfrac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$

$= \dfrac{[H_3O^+]^2}{(3.5 \times 10^{-3})\ M}$

$[H_3O^+] = \sqrt{(1.05 \times 10^{-10})(3.5 \times 10^{-3})} = 6.06 \times 10^{-7}$

pH = 6.22

6 a $K_a = \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

b $K_b = \dfrac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$

c $K_w = K_a \times K_b$

$K_a \times K_b$

$= \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \times \dfrac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$

$= \dfrac{\cancel{[CH_3COO^-]}[H_3O^+]}{\cancel{[CH_3COOH]}} \times \dfrac{\cancel{[CH_3COOH]}[OH^-]}{\cancel{[CH_3COO^-]}}$

$= [H_3O^+][OH^-] = K_w$

So $K_w = K_a \times K_b$

d As $K_w = [H_3O^+][OH^-]$

So $OH^- = \dfrac{K_w}{H_3O^+}$ or $H_3O^+ = \dfrac{K_w}{OH^-}$

The concentration of hydronium ions in a solution can be determined from the concentration of the base and K_w. As the concentration of the base increases the concentration of the acid decreases and the ratio remains K_w.

7 a $CH_3COOH(l) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

b $K_a = 1.74 \times 10^{-5} = \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

$[H_3O^+]^2 = 1.74 \times 10^{-5} \times [CH_3COOH]$

$[H_3O^+] = \sqrt{(1.74 \times 10^{-5} \times 0.4)} = 0.002638$

pH = 2.58

Question set 2.4

4 a $K_a = 6.31 \times 10^{-5} = \dfrac{[Brb^-][H_3O^+]}{[HBrb]}$

b At end point:

$\dfrac{[Brb^-]}{[HBrb]} = 1$

$[H_3O^+] = 6.31 \times 10^{-5}$

pH = 4.2

5 a pH of 8.2 has a $[H_3O^+] = 10^{-8.2}$

pH of 8.1 has a $[H_3O^+] = 10^{-8.1}$

% change = 25%

6 $K_a = \dfrac{[P^-][H_3O^+]}{[HP]} = 5 \times 10^{-10}$

the ratio $\dfrac{[P^-]}{[HP]} = 5 \times \dfrac{[10^{-10}]}{[H_3O^+]}$

a At pH 6: $\dfrac{[P^-]}{[HP]} = 5 \times \dfrac{10^{-5}}{10^{-6}} = 5 \times 10^{-4}$

Predominant species HP.

b At pH 11: $\dfrac{[P^-]}{[HP]} = 5 \times \dfrac{10^{-10}}{10^{-11}} = 5 \times 10^{1}$

Predominant species P^-.

Chapter review questions

5 a $K_a = \dfrac{[F^-][H_3O^+]}{[HF]}$

b $K_a = \dfrac{[H_3PO_4^{2-}][H_3O^+]}{[H_3PO_4]}$

c $K_a = \dfrac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]}$

6 $K_a = \dfrac{[CHOO^-][H_3O^+]}{[CHOOH]} = \dfrac{[\text{products}]}{[\text{reactants}]}$

8 Order from weakest to strongest is: Acid D, C, A, B.

9 a pH = 1.3

b $\dfrac{10^{-14}}{0.02} = 5 \times 10^{-13}$ pH = 12.3

10 pH = 1.31, $[H^+] = 10^{-1.31} = 0.0490$

$[SO_4^{2-}] = [H_3O^+]$

$K_a = \dfrac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = \dfrac{[H_3O^+]^2}{[HSO_4^-]} = \dfrac{0.0490^2}{0.25}$

$= 0.0096$

11 pH = 6.14, $[H^+] = 10^{-6.14} = 7.24 \times 10^{-7}$

$[H^+] = [OH^-]$

$K_w = [H^+][OH^-] = [H^+]^2 = (7.24 \times 10^{-7})^2 = 5.25 \times 10^{-13}$

12 pH 13 $[H_3O^+]$ is 10^{-13}, so $[OH^-] = 10^{-1} = 0.1$,
$n = cV = 0.1 \times 0.750 = 0.075$ mol

$n = \frac{m}{M}$, $m = nM = 0.075 \times (23 + 17) = 3.0$ g

15 pH = 2.4, $[H^+] = 0.00398$, $[H^+] = [HCOO^-]$ and [HCOOH] is 0.10 M

$$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]} = \frac{0.00398^2}{0.1} = 1.6 \times 10^{-4}$$

16 a $HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+$

$\frac{HCO_3^-}{CO_3^{2-}}$ acid and conjugate base

$\frac{H_2O}{H_3O^+}$ base and conjugate acid

b $K_a = 4.7 \times 10^{-11} = \frac{[HCO_3^-][H^+]}{[CO_3^{2-}]}$

$$\Rightarrow [H^+] = 4.7 \times 10^{-11} \times \frac{[CO_3^{2-}]}{[HCO_3^-]}$$

$$= 4.7 \times 10^{-11} \times \frac{0.4}{0.25}$$

$$= 7.52 \times 10^{-11}$$

$pH = -\log[H^+] = 10.12$

17 a $K_a = \frac{[OH^-][H_3BO_3]}{[B(OH)_4^-]}$

b $10^{-pH} = [H^+]$, $[H^+] = 7.76 \times 10^{-12}$ M

$$[OH^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{(7.76 \times 10^{-12})} = 0.0013 \text{ M}$$

c $[OH^-] = [H_3BO_3] = 0.0013$ M

d $$K_a = \frac{[OH^-][H_3BO_3]}{[B(OH)_4^-]} = \frac{0.0013^2}{0.1} = 1.7 \times 10^{-5}$$

19 a $K_a = \frac{[CN^-][H_3O^+]}{[HCN]}$

b $K_a = 6.3 \times 10^{-10}$

$[H_3O^+] = \sqrt{(6.3 \times 10^{-10} \times 0.00010)} = 2.5 \times 10^{-7}$

pH = 6.6

c $$\frac{[CN^-]}{[HCN]} \times 100 = \frac{2.5 \times 10^{-7}}{0.00010 \times 100} = 0.25\%$$

Chapter 3

Question set 3.1

4 a Oxidation: $Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$

Reduction: $2H+(aq) + 2e^- \rightarrow H_2(g)$

b Oxidation: $Mg(s) \rightarrow Mg2+(aq) + 2e^-$

Reduction: $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

c Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Reduction: $2Ag + (aq) + 2e^- \rightarrow 2Ag(s)$

d Oxidation: $2I^-(aq) \rightarrow I_2(s) + 2e^-$

Reduction: $Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$

Question set 3.2

3 a (2, 6)

b (2, 8)

Question set 3.3

4 $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$

Question set 3.4

6 $Bi^{3+}(aq) + 3H_2O(l) \rightarrow BiO_3^-(aq) + 6H^+(aq) + 2e^-$

Chapter review questions

11 a $VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$

b $HNO_2(aq) + H_2O(l) \rightarrow NO_3^-(aq) + 3H^+(aq) + 2e^-$

c $CH_3CH_2OH(l) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$

Chapter 4

Question set 4.2

5 a $n_{NaHCO_3} = c_{NaHCO_3} \times V_{NaHCO_3}$

$= 0.135 \times 0.250 = 0.03375$ mol

$m_{NaHCO_3} = M_{NaHCO_3} \times n_{NaHCO_3}$

$= 84.01 \times 0.03375 = 2.84$ g

Question set 4.3

4 b $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

$n_{HCl} = c_{HCl} \times V_{HCl} = 0.0873 \times 0.02500$

$= 2.18 \times 10^{-3}$ mol

$n_{NaOH} = n_{HCl} = 2.18 \times 10^{-3}$ mol

$$c_{NaOH} = \frac{n_{NaOH}}{V_{NaOH}} = \frac{2.18 \times 10^{-3}}{0.03730}$$

$= 0.0585$ mol L^{-1}

5 a Methyl orange

b Sodium hydrogen carbonate solution

d $H_2SO_4(aq) + 2NaHCO_3(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$

e $n_{NaHCO_3} = c_{NaHCO_3} \times V_{NaHCO_3} = 0.145 \times 0.02235$
$= 3.24 \times 10^{-3}$ mol

$n_{H_2SO_4} = \frac{1}{2} \times n_{NaHCO_3} = \frac{1}{2} \times 3.24 \times 10^{-3}$
$= 1.62 \times 10^{-3}$ mol

$c_{H_2SO_4} = \frac{n_{H_2SO_4}}{V_{H_2SO_4}} = \frac{1.62 \times 10^{-3}}{0.02000}$
$= 0.0810$ mol L^{-1}

Question set 4.4

5 0.461 g

6 83.1%

7 Diprotic acid

Chapter review questions

10 a $Ba(OH)_2(aq) + 2HCl(aq) \rightarrow BaCl_2(aq) + H_2O(l)$

b Bromothymol blue

c Blue to yellow

11 a Hydrogen peroxide

c 0.490 mol L^{-1}

12 a A weak acid

b Acetic acid

c 8.5

13 26.75%

Chapter 5

Question set 5.1

5 Species B

Question set 5.2

4 a $E^\circ = +0.40$ V

b $E^\circ = +1.09$ V

c $E^\circ = +2.37$ V

8 a $Fe(s) \mid Fe^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$

b $Pt(s) \mid I^-(aq) \mid I_2(s) \parallel Fe^{3+}(aq), Fe^{2+}(aq) \mid Pt(s)$

Chapter review questions

7 a $Al(s) \mid Al^{3+}(aq) \parallel Fe^{2+}(aq) \mid Fe(s)$

b $2Cu^{2+}(aq) + 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 2Cu(s)$ $E^\circ = -0.89$ V
Cell voltage: −0.89V

Chapter 6

Question set 6.1

1 $1s^2 2s^2 2p^2$

Question set 6.2

1 a C_nH_{2n+2}

b C_nH_{2n}

c C_nH_{2n-2}

5 A alkyne; B alkene; C alkane

8 a Pentyne (or any of its isomers)

b Butane

c Nonene (or any of its isomers)

11 a $C_5H_8(g) + 7O_2(g) \rightarrow 5CO_2(g) + 4H_2O(g)$

b $C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$

c $CH_3CH_2{=}CH_2CH_3(g) + H_2O(g) \rightarrow CH_3{-}CH_3{-}CH_2OH{-}CH_3(l)$

d $CH{\equiv}CH(g) + Br_2(aq) \rightarrow CHBrCHBr(aq)$
ethyne bromine 1,2-dibromoethene
$HBrC{=}CHBr(g) + Br_2(aq) \rightarrow CHBr_2CHBr_2(aq)$

Question set 6.3

3 a 3-methylpentane

b 3-methylpentane

c 2,2-dimethylbutane

d 3-methyl-1-butene

e 2,4-dimethyl-2-pentene

f 4-methyl-2-pentyne

g 3,3-dimethyl-1-pentyne

5 Pair a

Questions set 6.4

2 Formula: C_6H_6

Question set 6.5

3 a −OH alcohol

b Carboxylic acid

c $-NH_2$ amine

d Ester

e Ketone

f Aldehyde

g Amide

Question set 6.6

5 a 1-hexanol

b 2-butanol

c 2-ethyl-2-butanol
d 3-methyl-2-butanol

9 a 2-butanone
b Methanoic acid
c Does not oxidise (tertiary alcohol)

Question set 6.7

5 a Ethanal
b 2-methylbutanal
c 2-pentanone
d 5-ethyl-3-heptanone

Question set 6.8

5 a Pentanoic acid
b Propanoic acid
c 2-methylbutanoic acid

6 b $2CH_3CH_2COOH(aq) + Na_2CO_3(aq) \rightarrow 2Na^+(aq) + 2CH_3CH_2COO^-(aq) + CO_2(g) + H_2O(l)$

7 a $CH_3CH_2CH_2COOH(aq) + NaOH(aq) \rightarrow Na^+(aq) + CH_3CH_2CH_2COO^-(aq) + H_2O(l)$
b $2Na(s) + 2HCOOH(aq) \rightarrow 2Na^+(aq) + 2HCOO^-(aq) + H_2(g)$

9 1-butanol

Question set 6.9

5 a Propyl ethanoate
b Butyl methanoate
c Propyl pentanoate

Question set 6.10

4 a Propanamine
b Triethanamine
c 3-methyl-2-butanamine
d Ethanamide
e N-methylethanamide
f N-propylpropanamide

Chapter review questions

4 c: C_5H_8

5 a Alkane; 2-methylbutane
b Alkene; *trans*-2-pentene
c Alkyne; 3,5-dimethyl-1-hexyne
d Alcohol; 2-butanol
e Amide; N-methylethanamide
f Carboxylic acid; propanoic acid
g Ester; ethylpropanoate
h Amine; propanamine
i Carboxylate anion; sodium butanoate
j Aldehyde; 2-methylpropanal
k Ketone; 4-octanone

Chapter 7

Question set 7.1

5 a $C_{14}H_{30} \rightarrow C_8H_{18} + C_6H_{12}$
b $C_6H_{12} \rightarrow C_3H_6 + C_3H_6$

Question set 7.4

1 Polyesters and polyamides

6 a (a) polyester; (b) polyamide

7 a (i) polyamide; (ii) polyester
c (i) amine, carboxylic acid;
(ii) alcohol, carboxylic acid
d (i) 1,5-diaminopentane, nonanedioic acid;
(ii) methylmethanethiol, butanedioic acid

Question set 7.5

2 Glycosidic link, $-C-O-C-$

3 The OH functional group

5 b $C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$

7 a $\%O = \left(5 \times \frac{16}{162}\right) \times 100 = 49.4\%$

$\%C = \left(16 \times \frac{12}{162}\right) \times 100 = 57.1\%$

b $MW = 300 \times 162 = 4.86 \times 104$

c $C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6$

d $(C_6H_{10}O_5)_{50} + 4\ H_2O \rightarrow 50C_6H_{12}O_6$

Question set 7.6

1 Peptide link

Chapter review questions

4 A
5 A
6 C
7 A
8 D
9 B
10 A
15 D
16 D

Chapter 8

Question set 8.2

1 From X-ray tubes or synchrotrons

2 X-rays

9 a & b

Question set 8.4

1 IR

3 Diatomic molecules (e.g. O_2 or $N_{2)}$

Chapter review questions

1 IR

5 Mass spectroscopy

12 1, due to symmetry

15 a 126.2 amu

17 a HPLC

b Mass spectroscopy

c NMR

Chapter 9

Question set 9.2

7 46.8%

8 96.4%

9 a $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

d Chlorine

Question set 9.3

3 Hydrogen

5 Oxidation half reaction:

$C_6H_{12}O_6(aq) + 6H_2O(l) \rightarrow 6CO_2(g) + 24H^+(aq) + 24e^-$

Reduction half reaction:

$C_6H_{12}O_6(aq) + 12H^+(aq) + 12e^- \rightarrow 3C_2H_5OH(aq) + 3H_2O(l)$

Question set 9.4

7 45.8%

Chapter review questions

11 a 88.8%

b 73.2%

GLOSSARY

absorption band a trough observed at a particular wavenumber in infrared spectra

accuracy dependent on the measuring instrument that is used; a mass balance that measures to 0.001 g is a more accurate instrument than a mass balance that measures to 0.1 g

acid dissociation equilibrium constant (K_a) the equilibrium expression of a weak acid

acid rain rain of low pH; results when chemicals such as sulfur and nitrogen oxides are released, leading to the production of acids in the atmosphere

activated complex an unstable state of high enthalpy where the bonds of the reactants have been broken but the new bonds of the products have yet to form

activation energy the energy needed to break the reactant's bond in order to form the products

addition polymer a polymer that forms by molecules adding together without the loss of any atoms

addition polymerisation the process of polymer formation by molecules adding together without the loss of any atoms

adsorb when atoms, ions or molecules adhere to a surface

aged refers to wine that has been stored to develop flavour and complexity. Wine can be aged in barrels or bottles. Red wines are aged for longer. White wines are drunk 'younger'.

alicyclic (cyclic) hydrocarbon a compound in which the carbon atoms have joined together to form a closed ring structure

aliphatic compound a hydrocarbon consisting of a chain or non-aromatic ring

alkane a chain hydrocarbon with only single carbon–carbon bonds

alkene a chain hydrocarbon with at least one carbon–carbon double bond

alkoxide an anion formed when an alcohol loses the H from the alcohol functional group

alkyne a chain hydrocarbon with at least one carbon–carbon triple bond

alpha helix secondary spiral protein structure held together by hydrogen bonds between the amide functional groups in the polypeptide chain

alpha-amino acid an amino acid in which the amine and carboxyl functional groups are attached to the same carbon atom; proteins can only form from alpha-amino acids

alpha-carbon the carbon atom of an amino acid to which is attached the amino and carboxyl functional groups, a hydrogen and a side chain

amide link the functional group produced by the condensation reaction between a $-NH_2$ functional group and a –COOH functional group

amine an organic family in which one or more atoms of hydrogen in ammonia (NH_3) are replaced by a carbon-containing group such as an alkyl group

amino acid monomer of a protein containing a carboxylic acid and amine functional group and an R group that may be polar, non-polar or ionic

amorphous substances that do not have an extended ordered arrangement of molecules

amphiprotic a substance that can gain or lose a hydrogen ion to act as an acid or a base

analogue a device or scale that gives a continuous measurement; the scale is continuous and may show any value in a range

analyte the solution of unknown concentration that will be analysed

anode the electrode where reduction occurs

anthocyanins molecules that give the colour to wine

antibodies proteins that recognise specific-shaped molecules and structures and bind to them; they help to fight disease in living organisms

aquatic relating to water

aramid a polymer containing amide linkages separated by a benzene ring

aroma the odour that originates from the grape; it is affected by the grape variety and growing season. Can also refer to the bouquet

aromatic hydrocarbon a hydrocarbon containing one or more benzene rings

astringency the sharp taste that makes the mouth dry or 'pucker'

atactic the random arrangement of side groups on both sides of a polymer chain

atmosphere the gases surrounding Earth

atom economy the percentage (by mass) of the reactants that form the desired product

atomic mass unit (amu) the approximate mass of 1 nucleon; it is measured in a mass spectrum and carbon-12 is assigned an amu of 12

back titration a method used to determine the mass or concentration of a substance that is not able to be determined directly

base peak the most common peak in a mass spectrum, it is assigned a value of 100% with other peaks relative to it

beta-pleated sheet secondary protein structure formed from two polypeptide chains held together by hydrogen bonds between the amide functional groups in the polypeptide chains

biofilm a stable colony of bacteria coating a material

biofuel an energy source produced from renewable sources such as crops

biopolymer a polymer made totally or in large part by living organisms

biosensor structure that can detect a change in a biological component such as a chemical or hormone

bottom-up approach molecular manufacturing starting with atoms and building up the desired structure by addition of atoms and manipulation of bonding

bound SO_2 sulfur dioxide that is combined with other substances such as sugars and anthocyanins; is not available to work as a preservative

bouquet the odours of the wine that arise due to the processing of wine, including fermentation and ageing

brine a salt solution, usually sodium chloride

buffer a solution of a weak acid and its conjugate base (or vice versa) that can counteract the addition of an acid or a base to maintain a constant pH

buffer capacity the extent to which a buffer is able to counteract the addition of an acid or a base

by-product a product resulting from a chemical process that is not the desired end product, but still has commercial value

carbohydrate a family of natural compounds made up of carbon, hydrogen and oxygen, many of which conform to the general formula $C_x(H_2O)_y$

carbon cycle the movement of carbon through the environment

carbonyl compound a compound containing the carbonyl group –C=O

carboxylic acid an acid with the functional group –COOH

catalyst a substance that increases the rate of a chemical reaction by providing an alternative pathway with a lower activation energy

catalytic cracking the process in which high molecular weight (high boiling point) fractions from crude oil are broken into lower molecular weight (lower boiling point) substances

cathode the electrode where oxidation occurs

cellular respiration the chemical reaction occurring in cells where oxygen and glucose react to form carbon dioxide, water and energy

chemical change a change that produces new substances

chemical shift (symbol δ (delta)) in NMR spectroscopy, it is the relative frequency that an odd nucleon nucleus will spin in a magnetic field compared to the standard tetramethylsilane (TMS), measured in ppm

chemical system the chemicals involved in a reaction

chemoselectivity the ability to produce one specific chemical product when several different chemicals can be the result of a reaction

chemosensor a molecule that can detect, indicate the presence of, and measure the concentration of a specific molecule or chemical

chirality a phenomenon where isomers have a non-superimposable mirror image

closed system a chemical system in which no substances are able to enter or leave

cold stabilisation a process that helps prevent sediments forming in bottled wine as it causes the precipitation of potassium hydrogen tartrate from the wine before bottling

collision theory the theory stating that for a reaction to proceed, the reactant particles must collide with sufficient energy and an appropriate orientation

colloidal suspension tiny particles of solids dispersed through a liquid, which cannot be separated by filtration through filter paper

combustion reacting with oxygen

composite a material made up of two or more different materials

condensation polymer a polymer that forms by the elimination of a small molecule (often water) when monomers join together

condensation polymerisation the process of polymer formation by the elimination of a small molecule (often water) when monomers join together

condensation reaction a reaction between two functional groups that results in the release of a small molecule (usually water)

conjugate acid (of a base) the acid that is formed when a base accepts a proton from an acid

conjugate base (of an acid) the base that is formed when an acid donates a proton to a base

conjugate pairs compounds that differ by one proton (H^+); for example, HCl/Cl^-

conjugated alternating double (or triple) and single bonds

contact process a series of reactions to produce sulfuric acid

continuous able to include any value, sometimes within a fixed range; for example, a rainbow is a continuous spectrum

convergent sequence a sequence in which the reaction steps run parallel before the reactants of two separate pathways are combined

copolymer a polymer consisting of two or more different monomers

corrosion the oxidation of a metal in the presence of oxygen to form the metal oxide

cross-linking the process by which two or more polymer chains are joined together to form an extended two-dimensional network

crystalline a substance with an ordered arrangement of atoms, ions or molecules in the solid

cycloalkane a cyclic hydrocarbon with only single carbon–carbon bonds

cycloalkene a cyclic hydrocarbon with at least one carbon–carbon double bond

cycloalkyne a cyclic hydrocarbon with at least one carbon–carbon triple bond

delocalised electrons valence electrons that are not restricted to specific bonds but which spread over several atoms in a chemical compound

dendrimer a molecule with a specific shape used to deliver drugs to a specific location in the body

dependent variable the variable that changes as a result of changes to the independent variable

detergent alkylbenzene sulfonate salt; hydrophobic hydrocarbon end (alkylbenzene) with a hydrophilic sulfonate ion end

diamine a molecule that has two amino ($-NH_2$) functional groups

dicarboxylic acid a molecule that has two carboxyl (COOH) functional groups

diffraction the pattern seen in X-ray crystallography

diol an alcohol molecule that has two hydroxyl (–OH) functional groups

dipeptide a molecule formed by the joining of two amino acids in a condensation reaction by a peptide link

diprotic a substance that can donate two protons to a base

disaccharide a carbohydrate such as sucrose, maltose and lactose, formed by a condensation reaction to join by a glycosidic link between two monosaccharides

discrete able to include only specific values, not continuous; for example, a line spectrum is a discrete spectrum

dispersion force weak intermolecular force resulting from momentary dipoles

dissociation reaction a reaction in which an ionic substance separates in a solution

dissolution the process of dissolving

DNA replication the process of copying of the DNA in cells

dynamic equilibrium a state in which the amount of reactants and products remains constant as the rates of the forward and reverse reactions are equal

electrochemical transforms energy between electrical energy and chemical potential energy

electrolyte a substance that conducts an electric current

electrolytic cell a type of electrochemical cell that transforms electrical energy to chemical potential energy; this is not a spontaneous reaction, it requires the input of electrical energy for the chemical reaction to occur

electrospinning a process that uses the electrostatic properties of fibres to create nano-sized fibres with specific properties

endothermic reaction a reaction that absorbs energy from the surroundings; the products have more energy than the reactants

endpoint the physical sign that indicates that the equivalence point has been reached; achieving the correct endpoint depends on using an appropriate method that will undergo a physical change at the appropriate point

energy density the energy released per unit mass or per unit volume of the battery

enhanced greenhouse effect the trapping of excess heat in Earth's atmosphere due to increased production of greenhouse gases such as carbon dioxide through human activity

enthalpy the total energy of a substance

enzyme a protein that catalyses chemical reactions in living organisms by orienting molecules in the correct manner and lowering the activation energy

equilibrium the state for a reversible reaction in a closed system when the forward and reverse reactions occur at the same rate

equilibrium constant (K) the value of the ratio between the concentration of the products and reactants

equilibrium expression the ratio of the concentration of products to reactants used to calculate the equilibrium constant

equivalence point the point when the reactants are present in the ratio shown by the mole ratio in the balanced chemical equation for the reaction

ester link the link between a carboxylic acid and an alcohol that forms an ester

esterification the reaction of a carboxylic acid with an alcohol to produce an ester

excess reactant or reagent the reactant that is left over when the limiting reactant is used up

exothermic reaction a reaction that releases heat energy to the surroundings due to the products having less energy than the reactants

extrapolation extension beyond the measured range of data to read or construct new data that have not been measured

falsifiable able to be disproved

fermentation an exothermic process that typically involves breaking down of carbohydrates in fruits and grains to form alcohols or acids in the absence of oxygen; in wine, yeasts convert sugars to ethanol and carbon dioxide

fingerprint region area of IR spectrum characteristic for a particular substance; corresponds to a wavenumber less than 1400 cm^{-1}

food chain a series of organisms that depend on the previous one as a food source

forward reaction the process of the reactants forming the products

free SO_2 sulfur dioxide that can work as a preservative

froth flotation a method for concentrating a metal ore through use of collectors and frothing agents; developed in Australia

fuel cell a galvanic cell that occurs where a fuel, such as hydrogen or methanol, is oxidised and oxygen is reduced releasing electrical energy

fullerene an allotrope of carbon shaped like a hollow ball or cage, with specific properties such as unique electrical conduction properties

functional group a special atom or group of atoms present in the families of organic compounds that imparts particular chemical and physical properties

galvanic cell a type of electrochemical cell that transforms chemical potential energy to electrical energy in a spontaneous chemical reaction

geometrical isomer an isomer resulting from the presence of a double bond around which carbon atoms cannot rotate, so they differ in the geometric relationship of substituent groups. Such isomers may also be referred to as *cis–trans* isomers

global warming the gradual increase in the overall temperature of Earth's atmosphere

glucophilic enzymes that react preferentially with glucose rather than fructose

glycosidic link the –C–O–C– group that is produced when two monosaccharides join

graphene an allotrope of carbon in a two-dimensional sheet that can be shaped into a variety of shapes such as nanotubes

green chemistry the area of chemistry that aims to reduce the impact of chemistry on the environment

Haber process the industrial process that combines nitrogen and hydrogen gases to produce ammonia on a large scale

half-equation when an equation has been split into its two components – the oxidation reaction or the reduction reaction

heat of reaction the amount of energy absorbed or released in a reaction

host–guest complex two molecules that fit together due to their specific chemical structure and molecular shape

hydrolysis reaction with water

hydrolysis the splitting of a molecule by addition of water, the reverse of a condensation reaction

hydronium ion the ion that forms when a proton is donated to a water molecule (H_3O^+)

hydrophilic attracting water; 'water loving' and capable of forming bonds with water

hydrophobic more attracted to particles of the same type than to water, usually immiscible with water; 'water-hating' and cannot bond with or dissolve in water

hypothesis a tentative prediction, usually based on an existing model or theory. Also a tentative explanation of an observation based on an existing model or theory

impervious does not allow particular substances to pass through

independent variable a variable upon which another variable depends

initiator a chemical species that reacts with a monomer to form an intermediate compound which enables the linking of monomers to form a polymer; it is incorporated into the polymer so is not a catalyst

inorganic compound a compound that is not organic

intercalated when one substance, lithium in the case given, is inserted between the layers of graphite

intermediate product of one reaction that is used as a reactant in the next reaction of a reaction pathway

interpolation to read or construct a new data point that has not been measured but is within the range of measured data

inverted sugar a sugar produced from the hydrolysis of the disaccharide sucrose to form the monosaccharides fructose and glucose

ionisation energy the energy required to remove one electron from an atom or ion of an element in a gaseous state

ionisation reaction a chemical reaction when an uncharged molecule becomes an ion

isoelectric point the pH at which an amino acid exists as an overall neutral zwitterion

isomers molecules with the same molecular formula, but with a different structure

isotactic the orderly arrangement of side groups on the same side of a polymer chain

isotope variant of an element that has a different number of neutrons, e.g. carbon-12 and carbon-14

latex a milky white liquid produced by some plants such as the rubber tree, which is used to make rubber

Le Chatelier's principle a principle that predicts the effect of changes to a system at equilibrium: if a change is made to a system at equilibrium, the system will react to partially counteract the change

limit of reading the minimum uncertainty in a measurement due to the precision with which the scale can be read

limiting reactant or reagent the reactant that is used up first and therefore limits the amount of product produced

line of best fit the line that most accurately fits the data, usually calculated using linear regression

linear sequence a sequence in which the reaction steps follow one after the other in a linear progression.

linearise to make linear; to convert into a form that can be described by a straight line

logbook the record of an experiment or investigation kept by the scientist performing the experiments; it is a legal record of the experiments and their results

maceration a process in which grape juice is in contact with seeds and grapes for a period of time; this allows colours and flavours to leach out

malolactic fermentation a second fermentation usually in red wine that reduces the acid content; bacteria in the sediments convert the diprotic acid malic acid into lactic acid

measurand the quantity being measured

mechanosynthesis another name for the orientation effect where specific functional groups or reactive sites are made to react together to produce the desired molecule

messenger RNA a molecule of RNA that is a copy of the DNA code so protein synthesis can occur

mineral a compound with a fixed chemical composition

model a representation of a system or phenomena that explains the system or phenomena. A model may be mathematical equations, a computer simulation, a physical object, words or other form

molecular ion (M^+) the largest peak (m/z) in a mass spectrum; generally corresponds to the molecular mass of the molecule

molecular manufacturing production of chemicals with specific shapes or chemical composition

molecular manufacturing production of chemicals with specific shapes or chemical composition

molecular recognition molecules recognise molecules by their shape or bonding and can selectively bind to these specific molecules

molecular self-assembly molecules are influenced by an outside factor such as a magnetic or an electric field or can spontaneously form a specific structure through formation of bonds between atoms or molecules

monomer a small molecule that combines with other monomers to make a polymer

monoprotic a substance that can donate one proton to a base

monosaccharide the simplest carbohydrate molecule that is a monomer of sugar and polysaccharides; commonly exists as a five- or six-membered ring with hydroxyl groups attached

must the combination of solids and liquids formed by crushing the wine grapes

myoglobin the oxygen-carrying protein used by mammalian muscle as a rapidly available source of oxygen

nanocontainers a nano-sized structure designed to store chemicals inside structures until the chemicals are required

nanocup a structure made from nanotubes that is shaped like a cup, designed to carry drugs inside the body

nanomachine an artificially created protein designed to perform a specific mechanical task

nanometre one-billionth of a metre, or 10^{-9} m

nanoparticle a particle with size around 1–100 nm, often with specific and useful properties

nanosensor a nano-sized structure used to detect chemicals or measure quantities of chemicals present in a particular environment

nanotechnology science and engineering that occurs on the nanoscale, around 1–100 nm

nanotube commonly made of carbon, a one-atom sheet of covalently bonded atoms rolled into a nanosized tube

neighbouring atom the carbon or atom next to the atom holding the protons (hydrogen atoms) in question

nitrogenous base a base found in DNA and RNA

non-polar having no charged ends or poles

n-type semiconductor a silicon lattice structure with extra elements allowing for free electrons to move within the structure

nucleating point a substance that will cause the formation of crystals in supersaturated solutions

nucleic acid an organic molecule, such as DNA and RNA, made of chains of nucleotides

nucleons a general name for both protons and neutrons

nucleotide composed of a nitrogenous base, phosphate group and a deoxyribose or ribose sugar, they join together to create DNA or RNA respectively

oenologist a winemaker

oenology the science of wine making

open system a chemical system in which substances are able to enter or leave

ore a mixture of chemicals that contains one in sufficient quantity to be economically viable to extract

organic compound a compound containing carbon (except carbonates, carbon dioxide and carbon monoxide)

orientation effect positioning of molecules prior to reaction so functional groups or reactive sites on the molecules line up, giving a specific final product

outlier a data point that does not fit the pattern shown by other measured data points

oxidant or oxidising agent a chemical species that causes another species to be oxidised

oxidation loss of electrons

oxidation state the number of electrons that an atom would have gained or lost to get to its present state; it assumes that each species is completely ionic

oxymyoglobin myoglobin protein that has reacted with oxygen

parallax error an error in measurement due to the observer's position relative to the measuring scale; if the reading is taken at an angle to the scale, then an error is introduced

parent peak also called the molecular ion

partial pressure the pressure exerted by a single gas in a gas mixture

passivating a metal that forms an impervious oxide layer on its surface, which prevents further corrosion

peptide link the functional group produced by the condensation reaction between a $-NH_2$ functional group and a –COOH functional group of different amino acids

percentage ionisation the percentage of the acid molecules that have ionised in water

percentage yield the percentage of the possible product that is actually produced

petrochemical industry industry that uses the components of crude oil (petroleum) as the starting material to produce a variety of different chemicals

phenolics aromatic compounds in which one or more hydroxyl groups (–OH) are attached to a six-carbon aromatic benzene ring

photosynthesis the process whereby organisms, particularly green plants, can use sunlight to produce nutrients (sugars) from carbon dioxide and water

physical change a change where no new substances are formed

phytoplankton microscopic organisms that float in large numbers in fresh or salt water

plagiarism presenting someone else's work, including their words or ideas, as your own

plastic a material that is capable of being moulded by heat and pressure

plasticiser a small molecule inserted between polymer chains to hold them further apart

polar having charged ends or poles

polyamide a polymer formed by a condensation polymerisation reaction between an amine group ($-NH_2$) and a carboxylic acid group (–COOH)

polyester a polymer formed by a condensation polymerisation reaction between an alcohol group (–OH) and a carboxylic acid group (–COOH)

polymer a substance consisting of long macromolecular chains

polymerisation a chemical reaction in which many small molecules combine to form one large molecule

polypeptide a long chain of amino acids that folds into secondary and tertiary protein shapes through the use of intermolecular forces

polyphenols a group of aromatic compounds that comprise many phenol molecules covalently bonded

polyprotic a substance that can donate more than one proton to base

polysaccharide a high molecular mass condensation polymer such as starch and cellulose, made from monosaccharides

precision the variation in repeated measurements, or the uncertainty of a measuring device

pressing the process of extracting juices from grapes and must; removes the skin and seeds from the wine

primary alcohol an alcohol in which one carbon atom is bonded to the carbon atoms attached to the –OH group

primary data data that you have measured or collected yourself

primary standard a solution of accurately known concentration that remains stable under common laboratory conditions for extended periods of time

protecting group a part of a molecule that temporarily forms to prevent a functional group from reacting

protein a high molecular mass copolymer resulting from condensation polymerisation reactions between amino acids

protein synthesis joining of amino acids to form chains, which fold in specific orientations to form a protein

protonate addition of a proton to a functional group, usually resulting in a positively charged functional group

p-type semiconductor a silicon lattice structure with elements that create space for an electron to be added to the structure

pyrolysis a process of decomposition of a substance at high temperatures

qualitative measurement a measurement with descriptive or non-numerical results

quantitative measurement a measurement with a numerical value

quinones organic compounds that have a six-membered ring with two –C=O groups in the ring; they are derived from aromatic compounds such as benzene

radical a molecule with an unpaired electron; it is highly reactive

random error a variation that affects a measurement in a random way so that the measurement is as likely to change in any one direction as in any other

raw material a material used in a chemical process that is readily available but not highly processed, including air, coal and sand

reaction mechanism the sequence of chemical reactions for an overall chemical change (reaction pathway)

reaction pathway the sequence of chemical reactions for an overall chemical change (reaction mechanism)

redox reaction a reaction that involves the oxidation of one species and the reduction of another species

reductant or reducing agent a chemical species that causes another species to be reduced

reduction gain of electrons

reference the source of a specific piece of information or quotation

reflux process of extended heating of a mixture without any loss of reactants and products

relative atomic mass (A_r) (RAM) the relative atomic mass of an element; the weighted average of the masses of the isotopes on a scale on which a carbon-12 atom has a mass of exactly 12 units

reliable highly likely to be true; a trustworthy source of information or reproducible data

renewable reactant a reactant that is renewable

reproducible giving the same result, within uncertainty, when repeated measurements are made

research question the specific question that a particular experiment or investigation is attempting to answer

residual sugar the sugars remaining in wine after fermentation. Some sugars cannot undergo fermentation. If fermentation is stopped early, then the unreacted sugars will also be included in the residual sugar

resin material used in the production of artificial proteins, holds the amino acids in the correct orientation so they join in the desired manner

resolution the limit of reading or precision of a measuring device

respiration the conversion of sugars into carbon dioxide and energy in living organisms

resveratrol a phenolic compound found in grape skins and seeds and is believed to have health benefits

retrosynthetic analysis a process for determining the reaction pathway for a synthesis reaction that involves starting with the product and working backwards by identifying simpler substances

reverse reaction the reaction in which the products form the reactants

reversible reaction a reaction in which the reactants become products and the products become reactants

ribosome a natural molecular machine that produces proteins through protein synthesis

rust hydrated iron(III) oxide ($Fe_2O_3.xH_2O$)

salt bridge allows the movement of ions to complete the circuit in a galvanic cell

saponification the reaction between an ester and a hydroxide ion to form an alcohol and a carboxylate anion

saturated a solution that contains the maximum amount of the substance dissolved in the solvent (usually water)

saturated compound an organic compound with only single bonds between carbon atoms

scatter graph a graph or plot showing data points, without a line joining the points, and used to demonstrate or determine a mathematic relationship between variables. The axes are defined by the variables

secondary alcohol an alcohol in which two carbon atoms are bonded to the carbon attached to the –OH group

secondary data data or information that has been collected by someone else

secondary interactions bonds that occur between molecules, including hydrogen bonds, dipole–dipole interactions and dispersion forces, also called intermolecular forces

self-ionisation constant (K_w) the equilibrium expression that shows water ionising into two ions

semipermeable allows some substances to pass through but not others

shielding the net effect of the electron shells and the neighbouring nuclei have on local electrical field felt by the proton or odd number nucleon

soap a salt of a fatty acid; hydrophobic hydrocarbon chain with a hydrophilic carboxylate ion end

solubility the amount that is able to dissolve in a given volume of the solvent (usually water)

spin–spin coupling the change in the local electrical field due to the presence of protons on the neighboring carbons

splitting the pattern seen in high-resolution NMR spectra due to the protons of the neighbouring atoms

stabiliser a substance used to inhibit a chemical reaction

standard drink the volume of a drink that contains 10 grams of ethanol when measured at 20°C

steady state a state in which the properties remain constant

stereoisomers isomers that are a mirror image of each other

stereoregular polymer a polymer with an ordered arrangement of side groups along the carbon backbone

strong acid an acid that readily donates a proton to water; K_a is large

substituent an atom or group of atoms that takes the place of (substitutes for) hydrogen on a parent carbon in a hydrocarbon molecule

supramolecular chemistry chemistry focusing on the interactions between groups of molecules

surfactant an agent such as a detergent that reduces the surface tension of liquids so that the liquid spreads out

surroundings substances around the chemical system but not involved in the reaction

syndiotactic the alternating arrangement of side groups on each side of a polymer chain

synthesise to make something; with respect to chemistry, to produce a specific product

systematic error an error that acts to give a consistent offset in data; for example, a zero error

tannin a group of compounds that comprises many phenol molecules; they can bind with other molecules and are responsible for the astringency of wine. This group is important for the ageing of wine

terrestrial relating to land

tertiary alcohol an alcohol in which three carbon atoms are bonded to the carbon attached to the –OH group

tetramethylsilane (TMS) the standard used in NMR spectroscopy that is considered to have a zero shift; the protons (hydrogen atoms) present have the maximum shielding

theory a collection of models and concepts that explain specific systems or phenomena. Scientific theories allow predictions to be made and hence are falsifiable

thermoplastic a polymer that can be melted and reshaped

thermosetting a polymer that cannot be melted and reformed

titrant the solution in a burette

titratable acidity the total amount of acid present in wine as determined by titration

titration a type of volumetric analysis that determines the equivalence point

top-down approach molecular manufacturing starting with larger substances and breaking them down into smaller, more useful substances

transesterification the process of reacting a triglyceride with an alcohol to form an ester and glycerol

transfer RNA moves amino acids into place so they can be joined in a ribosome during protein synthesis

triglyceride a large molecule formed from the reaction between glycerol and three fatty acids

triprotic a substance that can donate three protons to a base

trough an absorption band in an IR spectra

true value the exact value of a measurand; an idealisation as all measurements have uncertainty and many measurands have values that vary

uncertainty an estimate of the range of values within which the 'true value' of a measurement or derived quantity lies

unsaturated compound an organic compound containing one or more multiple bonds

valid results that are affected only by a single independent variable and hence are reproducible

variable something that can change or be changed, as distinct from a constant, which does not

viniculture a specific branch of horticulture that involves the science, production and study of grapes for wine production

volumetric analysis determining the concentration of a sample by measuring the volumes of each reactant that reacts and knowing the concentration of the other reactant

vulcanisation the process of strengthening a material such as rubber by combining it with sulfur and other additives and then applying heat and pressure

waste product product from a chemical process that has no commercial value or is toxic or dangerous

wavenumber the inverse of wavelength; number of waves per centimetre; used in IR spectra

weak acid an acid in which only a small proportion of the molecules will donate their proton; the K_a is small

yield the amount or percentage of the possible product that is actually produced

zeolite an inorganic compound of aluminium, silicon and oxygen with metal ions, used for cracking alkanes into shorter chains

zwitterion an ion that has a positive and a negative charge on the same group of atoms; can be formed from compounds that contain both acidic and basic groups in their molecules, such as amino acids

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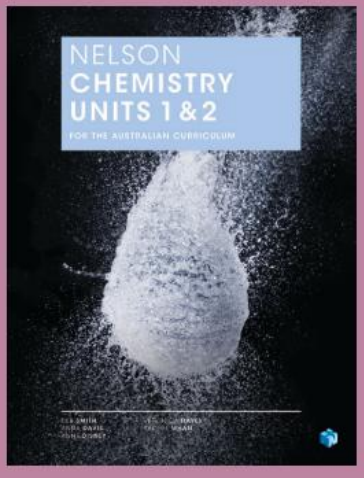
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